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Geochemical behaviour of naphtalene, phenanthrene and pyrene in soil: Kinetic and equilibrium sorption studies

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Abstract: The batch experiments were used to determine the sorption properties of three polycyclic aromatic hydrocarbons (naphtalene, phenanthrene and pyrene). One agricultural soil, arenic Fluvi-Gleyic Phaeozem, was used. The experimental sorption isotherms were nonlinear and fitted well to the Freundlich sorption model. Impact of soil contact time on the sorption properties of PAHs was evaluated by measuring the distribution relationships at soil contact time of 2 h, 1, 2 (3 for pyrene) and 21 d. The results indicated that sorption equilibrium for naphtalene, phenanthrene and pyrene was reached within 1, 2 and 3 d, respectively. This suggested more hydrophobic PAHs could exhibit slower sorption kinetics than less hydrophobic PAHs. Water solubility and *n*-octanol – water partition coefficient were main factors affecting sorption properties of PAHs studied. The effect of nonlinear sorption behaviour of PAHs on the mobility in a soil was also discussed.

Key words: polycyclic aromatic hydrocarbons (PAHs), soil, soil contact time, sorption.

1. Introduction

Many studies indicated that sorption of hydrophobic organic chemicals in soils was not rapid and linear, despite past assumptions to the contrary. Deviations from the sorption linearity and equilibrium have major impacts on contaminant transport and fate models (Appert-Collin et al., 1999; Spurlock et al., 1995). A study by Ball & Roberts (1991) indicated that sorption of perchloroethylene and tetrachlorobenzene was a slow process that could take tens and hundreds of days to reach equilibrium, respectively. They also indicated that sorption of less hydrophobic perchloroethylene was more rapid than more hydrophobic tetrachlorobenzene. Similarly, Xing & Pignatello (1996) showed that Freundlich coefficients could increase 1.3 to 10 times between 1 and 180 d and that sorption isotherms become more nonlinear with increased soil contact time. Conversely, Sharer et al. (2003) observed no increase in chlorobenzene uptake by three soils between 24 h and 14 mo. The results summarized in studies by Luthy et al. (1997) and Pignatello & Xing (1996) indicate that slow sorption of organic chemicals in soils contributes significantly to the overall sorption and that could take a few days to years depending on solute-sorbent system.

Sorption of organic chemicals as polycyclic aromatic hydrocarbons (PAHs) in natural porous solids was often viewed as only linear process (Karickhoff et al., 1979; Means et al., 1980; Schwarzenbach & Westall, 1981). Thermodynamically, the sorption of these compounds is treated as phase partitioning between the aqueous solution and the soil organic matter viewed as an organic phase into which the sorbate is transferred. Rather than an surface adsorption process, sorption of hydrophobic

organic chemicals may be described as an absorption process. This is especially true when concentrations of organic chemicals are sufficient to effectively saturate surface adsorption sites (Chiou & Kile, 1998; Chiou et al., 2000). This concept leads to definition of organic carbon distribution coefficient K_{OC} which is strongly dependent on the solute solubility in water S_w and *n*-octanol – water partition coefficient of the solute K_{OW} . Thus, it can be expected that K_{OC} value remains constant for a given hydrophobic organic chemical in natural solids with approximately the same nature of organic matter. Many experimental studies have shown that the amount of solute sorbed by soils S only depends on the total soil organic carbon content f_{OC} and on the nature of the solute through K_{OC} and its concentration C : $S = (K_{OC} \times f_{OC}) \times C$. The assumption that K_{OC} is independent of the nature of soil organic matter and the solute concentration in water has been questioned. However, it is believed that the effect of the nature of soil organic matter consisting mainly of humic substances on the K_{OC} is not large (Kile et al., 1999; Rutherford et al., 1992). Similarly, the magnitude of the solute concentration on the K_{OC} of "normal" soils is not large. The observed low-concentration values with such soils usually lie within a factor of three of those observed at higher concentrations, except at extremely low aqueous concentrations ($< 0.01 \times S_w$); (Allen-King et al., 2002).

The objective of this study was to evaluate sorption properties of three representative polycyclic aromatic hydrocarbons in one soil using batch experiments. Distribution relationships for naphtalene, phenanthrene were measured after 2 h, 1, 2 and 21 d and for pyrene after 2 h, 1, 3 and 21 d.

2. Materials and methods

Soil. Surface soil sample (5–30 cm depth) from a field near Stupava was collected, air-dried and passed through a 2-mm-diameter sieve. Selected properties of soil are listed in Tab. 1. The particle size analysis was determined following the pipette method by Novák. Soil pH was measured in a 1:2.5 (wt:wt) soil-water suspension and a 1:2.5 soil-1 M KCl solution suspension. Organic carbon content was determined using a wet oxidation method by Ľurin. Mineralogical composition of soil clay was determined by X-ray diffraction method.

Solutes. Naphtalene, phenanthrene and pyrene all with purity higher than 97 % were used. Physico-chemical parameters of the selected polycyclic aromatic hydrocarbons are shown in Tab. 2. Primary stock solutions of phenanthrene and pyrene were prepared by dissolving appropriate amount of each chemical in HPLC-grade methanol, and a series of stock solutions of various concentrations were prepared by sequential dilution of the primary stock solutions. Primary stock solution of naphtalene was prepared by dissolving it in a background solution consisting of deionized water (Milli-Q Plus) and 10^{-4} M HgCl_2 to prevent biological activity. Initial aqueous solutions were prepared by mixing a background solution and a desired volume of a stock solution. In all initial aqueous solutions methanol content was less than 1 vol. %.

Sorption experiments. The sorption of the three PAHs was investigated using laboratory batch sorption method. Each batch experiment involved adding soil (4 g of soil for naphtalene and phenanthrene and 1 g for pyrene) and 40 ml of initial aqueous solution into 50 ml glass vials. Glass vials were capped with glass lids and enclosed in aluminium foil to prevent photodegradation. The vials were agitated on a horizontal shaker for 2 h, 1, 2, 21 d (naphtalene and phenanthrene) and 2 h, 1, 3, 21 d (pyrene). An aliquot of soil suspension was withdrawn from each vial at appropriate soil contact time and then added into centrifuge tubes. The soil suspensions in tubes were centrifuged at 10 000 rpm for 5 min and a clear supernatants were taken for analysis. In each set of experiments, 4 blanks without soil were prepared in the same way to estimate loss of solutes. Losses of naphtalene and phenanthrene were ~ 10 % and were taken into account for calculation of sorbed amounts by soil. Concentrations of PAHs in initial aqueous solutions as well as in clear supernatants after sorption were analysed on a reversed-phase HPLC (Hewlett-Packard model 1100, 5 μm , 2.1 \times 250 mm SUPELCOSIL LC-PAH 57945 column or HYPERSIL Green PAH column) with fluorescence detector (Hewlett-Packard 1046A). External methanol solution standards were used to establish linear calibration curves for fluorescence detector. The eluting solvent used was a mixture of acetonitrile and water. The average uncertainty for the measured concentrations was about ± 5 %. All experiments were performed in two replicates. Analysis was carried out by National Water Reference Laboratory for Slovakia, Bratislava.

Data modeling. The amounts of PAHs sorbed by the soil S ($\mu\text{g.kg}^{-1}$) were calculated from the difference

between the initial C_0 ($\mu\text{g.L}^{-1}$) and remaining (equilibrium) C ($\mu\text{g.L}^{-1}$) concentrations in solution $S = (C_0 - C) \times V/m$, where V (L) is the volume of aqueous solution and m (kg) is the weight of soil.

The data were fitted to the Freundlich sorption model $\log S = \log K_F + N \log C$, where K_F ($\mu\text{g}^{1-N} \cdot \text{L}^N \cdot \text{kg}^{-1}$) is the Freundlich sorption constant and N is the Freundlich exponent, an indicator of isotherm nonlinearity.

The sorption distribution coefficient K_D (L.kg^{-1}) for each solute-sorbent combination can be calculated by $K_D = S/C$. The organic carbon distribution coefficient K_{OC} (L.kg^{-1}) is described by $K_{OC} = K_D/f_{OC}$, where f_{OC} is the fraction of organic carbon of the soil ($\text{OC}\%/100$). At a solute concentration of unity, K_D equals K_F and $K_{OC} = K_F/f_{OC}$.

3. Results

The measured distribution relationships with best-fit lines from the Freundlich sorption model for PAHs studied are in Fig. 1. Sorption of naphtalene did not exhibit increases in sorption from 1 to 2 d (Tab. 3), while phenanthrene did show a significant increase in K_D and K_F values between 1 and 2 d of soil contact times (Tab. 3). After 21 d, sorption of phenanthrene showed an increase in K_D compared to the corresponding value at 1 d, but K_D for naphtalene remained unchanged. Sorption of pyrene showed an increase in K_D and K_F values between 1 and 3 d of soil contact times, whereas there was observed no increase in sorption from 3 to 21 d (Tab. 3).

The Freundlich model regressions indicated nonlinear pattern of the measured distribution relationships as showed by Freundlich exponent values less than 1.0. The distribution relationships for all three PAHs were linear at 2 h of soil contact time (Tab. 3). However, they became nonlinear at 1 d of soil contact time and Freundlich exponent values remained unchanged after 1 d. When there was no longer observed a change in sorption of PAHs studied, the measured distribution relationships could represent equilibrium sorption isotherms (Fig. 2).

There seems to be agreement between organic carbon distribution coefficients K_{OC} obtained from K_D at relatively high solute concentration in water ($> 0.01 \times S_w$) and those estimated from the solute's K_{OW} value according to the regression equations of Karickhoff (1981), Karickhoff et al. (1979) and Xia (1998 in Allen-King et al., 2002) (Tab. 3, Fig. 3). The obtained data indicated that the sorption of PAHs was positively correlated to the solute's K_{OW} values and negatively correlated to their water solubilities (Fig. 2).

4. Discussion

Effect of soil contact time

The results indicated that there was somewhat an effect of solute's properties on the sorption equilibrium. The K_D and K_F values for phenanthrene and pyrene showed a significant increase from 1 d to 2 d and 3d, respectively and remained constant at 21 d. On the other hand, the K_D and K_F values for naphtalene were

Tab. 1. Physical and chemical properties of the agricultural soil.

Class	Clay (%)	Silt (%)	Sand (%)	Texture	pH _{H2O}	pH _{KCl}	OC (%)	Main clay minerals
Arenic Fluvi-Gleyic Phaeozem	11	15	74	sandy loam	7.96	7.38	1.19	Illite > Chlorite

Tab. 2. Physical and chemical parameters of the selected PAHs at room temperature.

	Naphtalene	Phenanthrene	Pyrene
Molecular weight (g.mol ⁻¹)	128	178	202
Melting point (°C)	81	100	156
Heat of fusion (kJ.mol ⁻¹) ^b	19.3	18.6	17.6
Molar volume (cm ³ .mol ⁻¹) ^a	111	152	159
Solubility parameter (J.mol ⁻¹) ^{1/2b}	41.4	40.1	44.3
Water solubility (mg.l ⁻¹) ^{a, b}	31.7	1.29	0.135
logK _{OW} ^b	3.36	4.57	5.18

^aValues as cited in Xia & Ball (1999). ^bFrom Chiou et al. (1998).

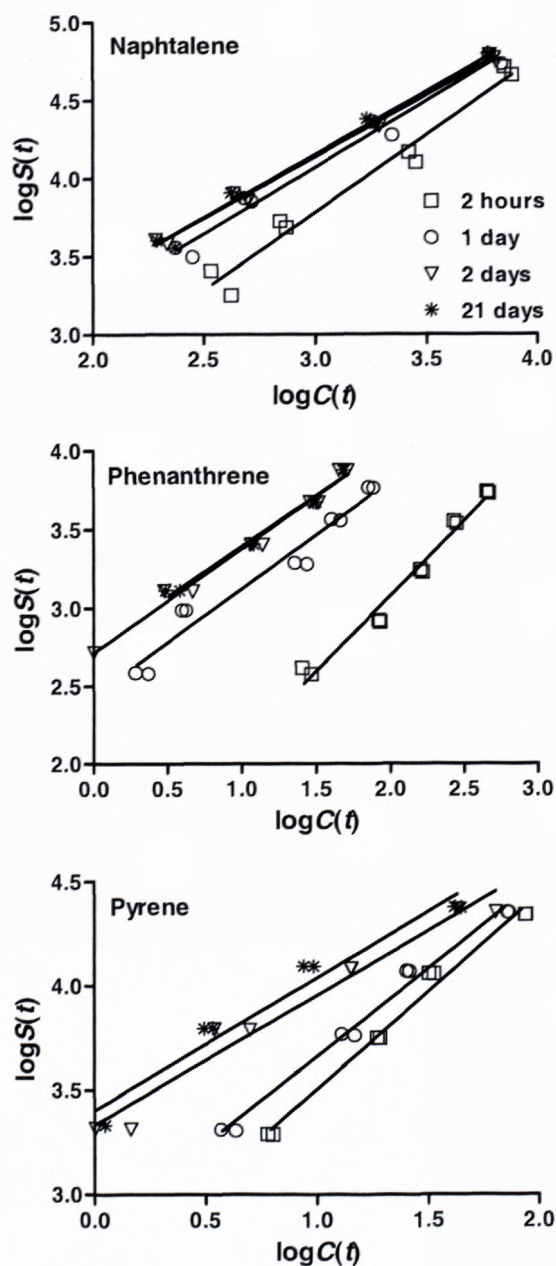


Fig. 1 Measured distribution relationships for naphtalene, phenanthrene and pyrene at different soil contact times.

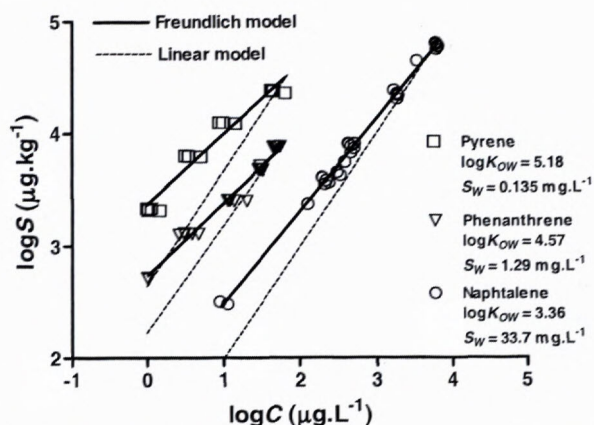


Fig. 2. Sorption isotherms for naphtalene, phenanthrene and pyrene with best-fit lines from the Freundlich sorption model (solid lines). The dashed lines represent the linear sorption model.

unchanged from 1 to 2 d. The limited data set provided here demonstrates that the sorption equilibrium of naphtalene, phenanthrene and pyrene was reached within 1, 2 and 3 d, respectively and that may be correlated to K_D . Naphtalene needs a shorter soil contact time to reach the sorption equilibrium (within 1 d) than phenanthrene and pyrene. Naphtalene has the lowest sorption coefficients and n-octanol – water partition coefficient of the PAHs studied (Tab. 3). Phenanthrene and pyrene have many times higher sorption coefficients and the K_{OW} values and there were necessary longer soil contact times to reach the sorption equilibrium. The results are similar with those of Ball & Roberts (1991) and Wu & Gschwend (1986). They demonstrated that the rate of approach to equilibrium for hydrophobic solutes was inversely correlated to their K_D or K_{OW} . This was attributed to the sorption-retarded pore diffusion of hydrophobic solutes. Brusseau & Rao (1989) showed that solutes with higher sorption coefficients should have slower sorption-desorption behaviour. The solute with higher K_D and K_{OW} equilibrated more slowly than that with lower K_D . On the other hand, Sharer et al. (2003) did not observed such relationships and suggested that specific interactions of the more polar compounds might be an important determinant of sorption kinetic behaviour.

Tab. 3. Sorption distribution coefficients K_D at higher solute aqueous concentrations ($C > 0.01 \times S_w$), organic carbon distribution coefficients K_{OC} and Freundlich parameters for naphthalene, phenanthrene and pyrene sorption by soil.

PAH	Contact time	K_D^a ($L \cdot kg^{-1}$)	$\log K_{OW}$	K_{OC} ($L \cdot kg^{-1}$)		Freundlich sorption model ^d	
				Experimental ^b	Calculated ^c	$\log K_F$ ($\mu g^{1-N} \cdot L^N \cdot kg^{-1}$)	N
Naphthalene	2 hour	6.05	3.36	983 1151 1202	692-1413	0.215-1.40	0.808-1.180
	1 day	11.7				1.12-1.90	0.729-0.978
	2 days	13.7§				1.59-1.95	0.730-0.849
	21 days	14.3				1.48-1.97	0.788-0.888
Phenanthrene	2 h	13.0	4.57	15630 16302	13305-22909	0.897-1.43	0.833-1.080
	1 d	107				2.28-2.60	0.563-0.806
	2 d	186#				2.62-2.81	0.583-0.742
	21 d	194				2.64-2.85	0.561-0.729
Pyrene	2 h	303	5.18	57731 70924	59020-93325	2.42-2.73	0.824-1.040
	1 d	413				2.69-2.95	0.748-0.939
	3 d	687#				3.20-3.46	0.500-0.742
	21 d	844				3.28-3.53	0.511-0.762

^aValues at $C > 0.01 \times S_w$ from best-fit parameters of the Freundlich sorption model. ^b $K_{OC} = K_D / f_{OC}$, where f_{OC} is the fraction of organic carbon (OC%/100). ^cValues from K_{OC} - K_{OW} correlations $K_{OC} = 0.989 \log K_{OW} - 0.346$ (Karickhoff, 1981), $K_{OC} = 1.00 \log K_{OW} - 0.21$ (Karickhoff et al., 1979) and $K_{OC} = 1.06 \log K_{OW} - 0.72$ (Xia, 1998 in Allen-King et al., 2002). ^d95 % confidence interval. §No significant increase in sorption from 1-day sample. #Significant increase in sorption from 1-day sample.

Equilibrium sorption behaviour

The equilibrium uptake of naphthalene, phenanthrene and pyrene by soil was affected by their hydrophobicity as reflected by the organic carbon distribution coefficients K_{OC} (Tab. 3, Fig. 2). This is well documented when the K_{OC} ratios for particular solute-solute combination to the corresponding K_{OW} ratios were compared:

$$K_{OC}^{Pyr} / K_{OC}^{Naph} = 60.9, K_{OC}^{Phen} / K_{OC}^{Naph} = 13.5,$$

$$K_{OC}^{Pyr} / K_{OC}^{Phen} = 4.51 \text{ vs. } K_{OW}^{Pyr} / K_{OW}^{Naph} = 66,$$

$$K_{OW}^{Phen} / K_{OW}^{Naph} = 16, K_{OW}^{Pyr} / K_{OW}^{Phen} = 4.07.$$

Many studies emphasized that the sorption of hydrophobic organic solutes was well positively correlated to n-octanol – water partition coefficient (Karickhoff, 1981; Karickhoff et al., 1979; Means et al., 1980; Seth et al., 1999). There was also agreement between organic carbon distribution coefficients K_{OC} obtained from K_D at relatively high solute concentration in water ($> 0.01 \times S_w$) and those estimated from the solute's K_{OW} value according to the regression equations of Karickhoff (1981), Karickhoff et al. (1979) and Xia (1998 in Allen-King et al., 2002); (Tab. 3, Fig. 3).

From the results presented in Fig. 2 and Tab. 4, it is evident that equilibrium sorption isotherms are nonlinear with N values ranging from 0.62 to 0.82 and that the Freundlich sorption model fits the equilibrium sorption data much better than the linear model. The observations are consistent with those of Carmo et al. (2000), Huang et al. (1997), Hwang et al. (2003), Toul et al. (2003) and Weber et al. (1992), but contradict linear behaviour observed by Karickhoff (1981), Karickhoff et al. (1979) and Means et al. (1980). Moreover, the results shown in Fig. 2 directly contradict the fact that linear isotherms are common at solute concentrations below 50 % of the solute water solubility S_w (Karickhoff, 1984). The linear sorption model has been widely accepted. According to

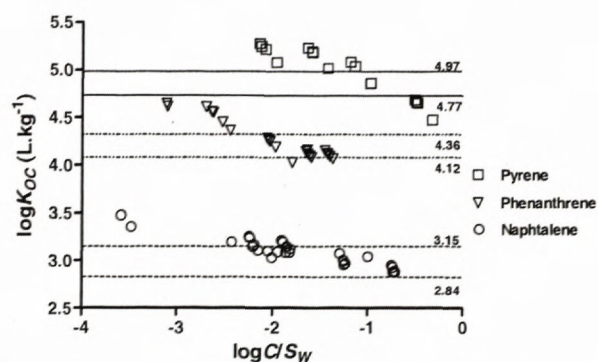


Fig. 3. The observed dependence of individually measured values of K_{OC} on the equilibrium solute concentration expressed by a ratio of equilibrium solute concentration to solute water solubility. The horizontal lines represent K_{OC} values predicted from K_{OC} - K_{OW} correlations by Karickhoff et al. (1979) and Xia (1998 in Allen-King et al., 2002).

this model, soil organic matter is the predominant sorbent in the sorption of hydrophobic organic chemicals by soils. Moreover, the sorption by soil organic matter occurs essentially by partitioning analogous to equilibrium extraction of an organic chemical from water by organic solvent (Chiou et al., 1979; Karickhoff et al., 1979). Linear isotherms are associated with this model and the slope is the linear distribution coefficient $K_{D,L}$, which is constant over the entire solute concentration range as well as K_{OC} . However, there were some limitations for this model as reflected by the equilibrium sorption data. The linear model could explain the equilibrium distributions of PAHs studied only at higher solute concentrations (Fig. 2 and 3). Conversely, the linear sorption model failed to consider the situation in the low relative solute concentrations (ratios of equilibrium solute concentration to solute water solubilities) (Fig. 2 and 3). The PAHs studied exhibited enhanced organic carbon distribution coefficients K_{OC} at low

Tab. 4. The equilibrium sorption data for naphthalene, phenanthrene and pyrene.

PAH	Freundlich sorption model		K_D at $C > 0.01 \times S_w^a$ (L.kg ⁻¹)	K_{OC} at $C > 0.01 \times S_w$ (L.kg ⁻¹)
	$\log K_F$ ($\mu\text{g}^{1-N} \cdot \text{L}^N \cdot \text{kg}^{-1}$)	N		
Naphtalene	1.66 (0.07) ^b	0.822 (0.027)	13.4	1126
Phenathrene	2.73 (0.06)	0.649 (0.05)	188	15798
Pyrene	3.37 (0.08)	0.622 (0.08)	755	63445

^aValues at $C > 0.01 \times S_w$ from best-fit parameters of the Freundlich sorption model.

^bNumber in parentheses is $\pm 95\%$ confidence interval.

relative concentrations ($C/S_w < 0.1$ - 0.001) than at high relative concentrations. The observed dependence of individually measured values of K_D and calculated values of K_{OC} ($= K_D/f_{OC}$) on the equilibrium solute concentration for each solute-sorbent system is one of the most striking properties of nonlinear isotherms. K_{OC} values calculated from individual isotherm points decreased appreciably as a function of equilibrium solute concentration (Fig. 3). For example, the K_{OC} value for naphthalene decreased from 2982 L.kg⁻¹ of OC at $C = 8.9 \mu\text{g.L}^{-1}$ to 759 L.kg⁻¹ of OC at $C = 6461 \mu\text{g.L}^{-1}$ and the K_{OC} for phenanthrene decreased from 43782 L.kg⁻¹ of OC at $C = 1.0 \mu\text{g.L}^{-1}$ to 11612 L.kg⁻¹ of OC at $C = 55 \mu\text{g.L}^{-1}$. The observed sorption behaviour of PAHs is inconsistent with that predicated using K_{OC} - K_{OW} correlations. For example, correlations given by Karickhoff (1981), Karickhoff et al. (1979), Means et al. (1982) and Xia (1998 in Allen-King et al., 2002) provided naphthalene's K_{OC} values of 955, 1413, 1096 and 692 L.kg⁻¹ of OC, respectively. K_{OC} values for phenanthrene predicated by these correlations were 14928, 22909, 17783, 13305 L.kg⁻¹ of OC, respectively. While some of these correlation-predicated K_{OC} values agree well with the K_{OC} values measured at higher equilibrium solute concentrations, all are at least 2.5 to 3 times lower than the K_{OC} values observed at lower C (1 - $10 \mu\text{g.L}^{-1}$); (Fig. 3).

Nonlinear sorption behaviour of PAHs observed in this study can be in accord with two recent concepts offering possible mechanistic interpretation of observed nonlinear sorption. Whereas one concept is based on the analogy between soil organic matter and synthetic polymers (Huang et al., 2003; LeBoeuf & Weber, 1997; Pignatello, 1998; Xing & Pignatello, 1997), the other looks for explanation in the heterogeneity of the soil organic matter and the presence of small amounts of high-surface-area carbonaceous material with high sorption capacities (Chiou et al., 2000; Karapanagioti et al., 2001; Kleineidam et al., 1999). In the soil organic matter-synthetic polymer analogy, a soil organic matter may comprise two principal domains as synthetic polymers: highly amorphous and swollen organic domain, analogous to a rubbery polymer and condensed, relatively rigid organic matrix, analogous to a glassy polymer (Weber et al., 2001). Sorption by rubbery polymers occurs by partitioning and generally yield isotherms that are essentially linear. Conversely, sorptions by glassy polymers occur by some type of adsorption and generally yield isotherms that are nonlinear and exhibit significantly larger sorption capacities. However, Chiou et al. (2000) and Chiou & Kile (1998) have argued that most of the nonlinearity is due to the presence of small amounts of high-surface-area

carbonaceous material (HSACM) with large sorption capacities and non-linear sorption behaviour of Langmuir type. HSACM, such as coal, carbonized woody fragments and soots are commonly present in soils and sediments and may result from fossil-fuel burning or burning of crop residues (Accardi-Dey & Gschwend, 2002; Allen-King et al., 2002; Cornelissen & Gustafsson, 2004; Yang & Sheng, 2003). The nonlinear sorption reported in this study could be attributed to the presence of trace amounts of carbonaceous material. The sampling site of soil sample used likely offers various sources for input of such carbonaceous material: vicinity of highway communications and intensive agricultural activities, e.g. field burning of crop residues. The two concepts presented here can be quite similar when it is considered that high-surface-area carbonaceous material may comprise properties of a glassy polymer.

Effect of nonlinear sorption on the mobility

One consequence of nonlinear sorption is that the mobility of a compound becomes dependent on the concentration. The relative mobility of a solute during equilibrium transport may be described using the retardation factor $R = 1 + (\rho/\theta) \times (\partial S/\partial C)$, where ρ (kg.L⁻¹) is the soil bulk density and θ (L.L⁻¹) is the volumetric water content.

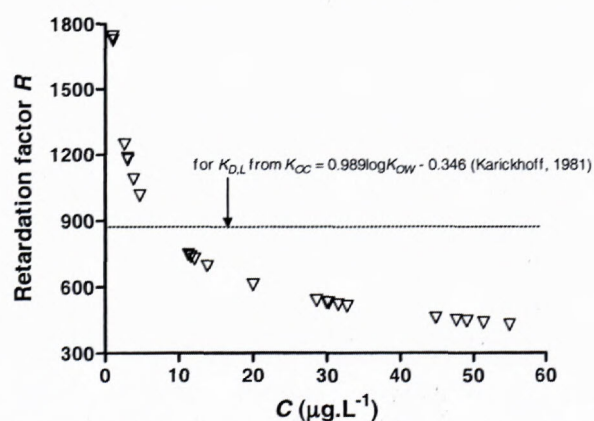


Fig. 4. The calculated change of retardation factor R with changing equilibrium solute concentration for phenanthrene. R is estimated using the idealized equation $R = 1 + (\rho K_F N / \theta) \times C^{N-1}$ (assuming soil bulk density of 1.5 kg.L^{-1} and volumetric water content of 0.30). The dashed line represents the value of R predicated from $K_{D,L}$ given by K_{OC} - K_{OW} correlation of Karickhoff (1981).

For the linear case, sorption coefficient $K_{D,L}$ is concentration independent, and therefore the retardation factor is also concentration independent. However, for the nonlinear

case, $R = 1 + (\rho K_F N / \theta) \times C^{N-1}$, which shows that the retardation factor is then concentration dependent. In Fig. 4, the dependence of the retardation factor on solute concentration for phenanthrene is plotted. Fig. 4 also illustrates the values of R predicated from $K_{D,L}$ given by the K_{OC} - K_{OW} correlation of Karickhoff (1981). The results show that the relative mobility of phenanthrene is significantly less at lower concentrations than at higher C and as predicated by the linear sorption model.

5. Conclusions

The study presented here demonstrates that the sorption equilibrium of naphthalene, phenanthrene and pyrene was reached within 1, 2 and 3 d, respectively and that may be correlated to K_D . Naphthalene needs a shorter soil contact time to reach the sorption equilibrium (within 1 d) than phenanthrene and pyrene. Naphthalene has the lowest sorption coefficients and n-octanol – water partition coefficient of the PAHs studied. Phenanthrene and pyrene have many times higher sorption coefficients and the K_{OW} values and there were necessary longer soil contact times to reach the sorption equilibrium.

The sorption isotherms of all three PAHs were nonlinear. Our results showed that the use of empirical correlations based on the linear sorption model failed to predict sorption coefficients at low solute concentrations. This is applied to solute concentration levels one order of magnitude or lower than the water solubility of a solute for soils containing mainly humus-like soil organic matter. Moreover, we emphasized the effect of nonlinear sorption behaviour on the mobility of PAHs in soil environment. Therefore, extrapolations of sorption behaviour observed in high solute concentrations in aqueous solution to low concentrations can be a source of considerable errors when estimating sorption-related fate and transport processes for hydrophobic organic chemicals.

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Investigation of the retention and release of the herbicide MCPA by soils and potential environmental impact to groundwater quality

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Abstract: In this paper, the retention and release of the herbicide MCPA by five different soil types was investigated at two initial concentrations in aqueous solution of 0.5 and 10 mg.l⁻¹. MCPA retention was positively correlated to soil organic matter content ($r = 0.958^{**}$ and 0.970^{**} for $C_0 = 0.5$ and 10 mg.l^{-1} , respectively). No other significant correlations between MCPA sorption and soil properties were found. Conversely, the release of MCPA from soils was negatively correlated to soil organic matter content. Experimental data indicate a primary role of soil organic components to control MCPA retention and release by soils. To estimate leaching potential of MCPA into groundwater, the measured K_{OC} values and average degradation half-life taken from literature were used. The calculated values of groundwater ubiquity score imply that MCPA is the mobile herbicide in all the investigated surface soils and has potential to contaminate groundwater, and hence it represents a threat to human health.

Key words: soils, MCPA, release, retention, groundwater quality

1. Introduction

Herbicides are widely applied for general weed control in agriculture. Increased herbicide use in agriculture has led to a general concern regarding their potential threat as contaminants in the soil and aquatic environment. Mobility of herbicides and their potential to migrate to the other compartments of the environment can be evaluated from sorption-desorption data (Bekbölet et al., 1999). Sorption, which removes a pesticide from the mobile phase of a soil, and hence retards its leaching, is one of the major processes influencing pesticide mobility in soil under laboratory conditions (Celis et al., 2005; Cox et al., 2001; Socías-Viciana et al., 1999), as well as under field conditions (Laabs et al., 2000, 2002). Herbicide sorption processes are undoubtedly one of the major determinants affecting also the persistence in soil and biological activity (Guo et al., 2000; Jensen et al., 2004). Herbicide sorption has to be accounted when predicting their transport in the subsurface and soils (Kodešová et al., 2005; Spurlock et al., 1995). Desorption process of herbicides is also important since it determines the release rate and the potential mobility of herbicides in soil (Boivin et al., 2005; Huang et al., 1998). Several studies showed that significant hysteresis occurred between sorption and desorption (Bekbölet et al., 1999; Boivin et al., 2005; Nemeth-Konda et al., 2002; Thorstensen et al., 2001a). Hysteretic sorption-desorption suggest that sorption of pesticides occurs with a limited degree of reversibility depending upon both the physico-chemical properties of the pesticides and soils (Boivin et al., 2005; Cooke et al., 2004; DeSutter et al., 2003). MCPA (4-chloro-2-methylphenoxyacetic acid) is a herbi-

cide widely used to control annual and perennial weeds, mostly in cereals (Tomlin, 2001). It belongs to the group of acidic herbicides with $pK_a = 3.07$. This herbicide is widely used in Slovakia due to its high selectivity. Although MCPA is only moderately toxic herbicide compared, for example, to triazine herbicides, monitoring its residue in water and soil is crucial because it can affect the nervous system upon adsorption through the skin and its prolonged inhalation can cause dizziness, burning in the chest and coughing (Crespín et al., 2001). Many studies emphasized a significant role of the soil pH to affect retention and release of acidic herbicides - retention is increased when soil pH is decreased (Boivin et al. 2005; Dyson et al. 2002; Spadotto & Hornsby, 2003; Thorstensen et al. 2001a). Total soil organic carbon content and its nature appears to be another important factor influencing sorption-desorption of acidic herbicides (Bekbölet et al. 1999; Haberhauer et al. 2000, 2001; Hiller et al., 2005; Socías-Viciana et al. 1999). In general, the phenoxyacid herbicide MCPA is weakly sorbed by soils (Sørensen et al., 2006) and susceptible to leaching (Jensen et al., 2004; Socías-Viciana et al., 1999). As a consequence of the low MCPA sorption, its relatively high water solubility and leaching potential and of the extensive use, it has been detected in European groundwater resources (GEUS, 2004).

Taking into account the above and fact that retention and release of weak organic acids has been less studied, the objective of this study was to determine these processes for the herbicide MCPA in six soils and to find the main soil properties governing retention and release of the herbicide by soils. The obtained sorption parameters were used to evaluate MCPA potential to leach and

contaminate groundwater. The sorption-desorption process was studied using batch experiments to obtain the sorbed and desorbed amounts of MCPA by soils.

2. Materials and methods

2.1. Chemicals

Analytical grade MCPA (purchased from Dr Ehrenstorfer GmbH) with 825 mg.l⁻¹ water solubility at 25°C and $pK_a = 3.07$ was used. Primary stock solution of MCPA was prepared by dissolving it in a background solution consisting of deionized and sterilized water (Milli Q+), 10⁻⁴ M NaN₃ to prevent biological activity and 0.01 M CaCl₂ to keep ionic strength constant. Initial aqueous solutions with 0.5 and 10 mg.l⁻¹ of dissolved MCPA were prepared by mixing a background solution and a desired volume of a stock solution.

Tab. 1. Selected characteristics of the soil samples.

Sample code	Soil type	Clay (%)	Silt (%)	Sand (%)	OC (%) ¹	pH _{H2O}	C _{HA} /C _{FA} ²
A1	Rendzina	11.13	51.00	37.87	4.586	6.93	1.09
A2	Pararendzina	9.080	39.17	51.75	2.486	7.86	1.07
A3	Fluvisol	15.32	46.76	37.92	1.922	7.99	1.12
A4	Luvisol	5.750	63.45	30.80	1.212	6.32	1.16
A5	Cambisol	22.08	59.60	18.32	0.893	6.76	0.72
A6	Fluvisol	4.050	21.35	74.60	0.600	8.20	nd ^a

¹OC – organic carbon content; ²C_{HA}/C_{FA} – soil humic and fulvic acid ratio; ^and – not determined. The soils are arranged according to their decreasing organic carbon content.

2.3. Sorption/desorption experiments

Studies of the sorption kinetics (with 1 and 100 mg.l⁻¹ of MCPA in 0.01 M CaCl₂ and 10⁻⁴ M NaN₃ aqueous solution) showed that MCPA sorption in calcareous Fluvisol (the A6 sample) reached an apparent equilibrium within 2 h (data not shown). Therefore, a 48 h equilibration time was considered to be adequate for sorption to attain true thermodynamic equilibrium. The experiments were carried out using the standard batch equilibration method. Prepared initial aqueous solution (5 ml) with 0.5 or 10 mg.l⁻¹ of MCPA was added to the soil (2 g). The concentrations are within the range of typical field application rates of 1–2.5 kg.ha⁻¹ (Tomlin, 2001). The mixture was shaken for 48 h and then centrifuged. Consequently, MCPA equilibrium concentration (C_e) in aqueous solution was determined by HPLC (High Performance Liquid Chromatography).

Desorption experiments followed immediately and were performed using aliquots of samples from the sorption experiments. The supernatant removed was replaced by the same amount of MCPA-free 0.01 M calcium chloride solution. The tubes were shaken for 48 hours. After centrifugation, desorbed amount of MCPA in solution was determined. Tubes containing only MCPA solution without soil were included to determine adsorption onto the surface of the tubes. All sorption and desorption experiments were performed at least in duplicate. No losses of MCPA due to adsorption onto the surface of the tubes or volatilization were observed.

2.2. Selected soils

Five soils were sampled in the surface layers (0–25 cm). They represent the surface A horizon and come from the Laborec river area (Eastern Slovakia). In addition, one soil was sampled from the subsurface (~ 200 cm) to determine whether there is a difference in MCPA sorption-desorption between surface soils and subsurface soil. This soil represents the subsurface C horizon of calcareous Fluvisol and comes from the Bratislava airport area (Western Slovakia). Physical and chemical characteristics of the soils used were determined according to Fiala et al. (1999) and are shown in Tab. 1. The soil organic carbon measured in this study represents humified materials consisting mainly of the humic acids, fulvic acids and humins (Tan, 1993).

The results from the sorption experiments were evaluated by the distribution coefficient K_d ($K_d = S_e/C_e$; l.kg⁻¹), where S_e is the amount of MCPA sorbed to the soil. The difference between initial (C₀) and equilibrium MCPA concentration was used to calculate the sorbed amount S_e (mg.kg⁻¹). The K_d values were corrected for soil organic carbon content (OC in %) by calculating K_{OC} ($= (K_d/OC) \times 100$). Desorption coefficients were calculated using this equation: $K_{des} = S_{des}/C_{des}$, where S_{des} (mg.kg⁻¹) is the amount of MCPA sorbed to the soil after desorption and C_{des} (mg.l⁻¹) is the analytically determined equilibrium amount of MCPA released into a solution.

2.4. Determination of MCPA in the aqueous solution

Concentrations of MCPA in initial aqueous solutions as well as in clear supernatants after sorption-desorption experiments were analysed on a reversed-phase HPLC (Hewlett-Packard model 1100, 5 µm, 4.6×125 mm LICHROSPHERE-100 RP column) with fluorescence detector (Hewlett-Packard 1046A). External solution standards were used to establish linear calibration curves for fluorescence detector. The mobile phase used was a mixture of acetonitrile and 0.05 M phosphate acid solution. The flow rate of this mobile phase was kept at the level of 0.4 ml per minute. The average uncertainty for the measured concentrations was about ±10 % and detection limit for the aqueous extracts was 0.02 mg.l⁻¹. Analyses were carried out at National Water Reference Laboratory for Slovakia, Bratislava under standard procedures of this laboratory.

3. Results and discussion

3.1. Effects of soil properties on retention and release of MCPA

Parameters that quantify retention and release of MCPA by soils at two initial concentrations are given in Tab. 2. MCPA was weakly sorbed by all soils used. The highest sorption (~ 30 %) was exhibited by the A1 soil sample with the highest organic carbon content among all the soil samples used, whereas the lowest sorption was observed in the A6 subsurface soil (only ~ 5 %) with the lowest organic carbon content (Tab. 2). The low extent of MCPA sorption could be attributed to the fact that MCPA would be negatively charged above pH 5 and consequently would be repelled by the predominantly negatively charged soil clay minerals or organic matter at pH values of the soils used (Dubus et al., 2001; Nicholls & Evans, 1991). Therefore, the interaction of the MCPA anions with the negatively charged soil mineral and organic matter surfaces at high pH of the soils will likely involve interaction with cationic species such as Ca^{2+} in salt bridge arrangements (Spark & Swift, 2002) or with Fe and Al oxo-hydroxides through specific and nonspecific electrostatic attractions (Vasudevan et al., 2002, 2004).

The obtained distribution coefficients (K_d) for the six soils at both MCPA initial concentrations were within 0.08–1.10 l.kg^{-1} . This corresponded to K_{OC} values be-

tween 15 and 35 l.kg^{-1} . Earlier studies of MCPA sorption on different soils with OC = 0.10–4.90 % gave K_d values in the range of 0.24–1.94 l.kg^{-1} with the corresponding K_{OC} values 27–156 l.kg^{-1} (Haberhauer et al., 2000; Socías-Viciano et al., 1999). Similar results were reported by Sørensen et al. (2006), who studied the sorption of MCPA in two soil profiles and their results showed that MCPA was weakly retained with $K_d = 0.03$ –1.89 l.kg^{-1} . The distribution coefficients for both C_0 increased with increasing soil organic carbon content. This was confirmed by a significant positive correlation between K_d and soil organic carbon content (Fig. 1). No other significant correlations between MCPA sorption and soil properties were found. The results indicate that soil organic matter played a main role in the MCPA sorption. Numerous laboratory studies have demonstrated an effect of soil organic carbon content on the sorption of MCPA and other weakly acidic herbicides (Al Kuisi, 2002; Bekbölet et al., 1999; Boivin et al., 2005; Hiller et al., 2005; Strebe & Talbert, 2001; Sørensen et al., 2006). The relatively constant K_{OC} values (Tab. 2), indicating similar sorption capacity of organic matter present in soils, and little or no difference between the observed K_{OC} and calculated ones (~ 10–35 l.kg^{-1}) from QASR relationship: $\log K_d = 0.93 \log K_{OW} + 1.09 \log f_{OC} + 0.32 C_{fa} + 0.25$ (Binstein & Devillers, 1994) are the another evidences for the primary effect of soil organic carbon content on the MCPA sorption.

Tab. 2. The sorption distribution coefficients (K_d), desorption coefficients (K_{des}), the amount of MCPA sorbed (P_{sorp}) and desorbed (P_{des}). Mean \pm experimental standard deviation.

Sample code	A1	A2	A3	A4	A5	A6
at MCPA initial concentration $C_0 = 10 \text{ mg.l}^{-1}$						
K_d (l.kg^{-1})	0.96 \pm 0.05 ^b	0.37 \pm 0.003	0.50 \pm 0.04 ^c	0.20 \pm 0.05	0.13 \pm 0.08	0.08 \pm 0.008
K_{OC} (l.kg^{-1})	21 \pm 1.10	15 \pm 0.10	26 \pm 1.90	17 \pm 4.00	15 \pm 8.50	13 \pm 1.60
P_{sorp} (%) ¹	27.7 \pm 1.04	13.0 \pm 0.07	15.7 \pm 0.01	7.40 \pm 1.77	4.94 \pm 2.74	3.01 \pm 0.29
K_{des} (l.kg^{-1})	2.97 \pm 0.11	1.76 \pm 0.05	1.59 \pm 0.14	0.56 \pm 0.12	0.42 \pm 0.37	0.27 \pm 0.12
P_{des} (%) ²	15.2 \pm 0.43	20.2 \pm 1.62	29.9 \pm 3.60	35.7 \pm 0.58	49.9 \pm 21.0	69.3 \pm 10.8
at MCPA initial concentration $C_0 = 0.5 \text{ mg.l}^{-1}$						
K_d (l.kg^{-1})	1.10 \pm 0.39	0.81 \pm 0.24	0.39 \pm 0.07	0.39 \pm 0.05	0.17 \pm 0.04	0.21 \pm 0.18
K_{OC} (l.kg^{-1})	24 \pm 8.50	32 \pm 9.60	21 \pm 3.60	32 \pm 4.40	19 \pm 5.00	35 \pm 30.0
P_{sorp} (%)	30.1 \pm 7.60	24.4 \pm 5.44	13.6 \pm 2.09	13.6 \pm 1.60	6.46 \pm 1.52	7.53 \pm 6.08
K_{des} (l.kg^{-1})	6.21 \pm 0.95	5.37 \pm 1.07	nd ^a	1.04 \pm 0.13	0.73 \pm 0.03	1.70 \pm 2.02
P_{des} (%)	12.8 \pm 3.34	10.9 \pm 0.03	nd ^a	34.5 \pm 17.4	51.5 \pm 4.12	55.5 \pm 33.2

¹ P_{sorp} – the percentage of MCPA sorption; ² P_{des} – the percentage of MCPA released; ^and – not determined; ^bThe average value from 7 samples ($n = 7$); ^cThe average value from 4 samples ($n = 4$); In all other cases, the experiments were performed in duplicate ($n = 2$).

Desorption (release) is of high importance because it affects the degradation rates and leaching behavior of a pesticide at different times and conditions. It is important to evaluate desorption since it determines the amount of herbicide that can be released back to aqueous solution and thus controls the final distribution of the herbicides in soil (Boivin et al., 2005; Haberhauer et al., 2000). In our study, the MCPA desorption from all the soils exhibited hysteresis, i.e. not all the amounts of MCPA sorbed by soils were desorbed within 48 hours (Tab. 2). Hysteresis is a common observed phenomenon, which can be attributed to irreversibility in the sorption process caused

by slow kinetics of desorption, diffusion-limited transport within the particles and/or irreversible binding of MCPA to the soil/sediment particles (Beck et al., 1996; Bekbölet et al., 1999; Cooke et al., 2004; Haberhauer et al., 2000; Jensen et al., 2004; Thorstensen et al., 2001a). When the sorption-desorption hysteresis occurs, there is a difference between the measured sorption and desorption distribution coefficients (K_d and K_{des} , respectively). The high K_{des} values indicate low desorption and vice versa (Bekbölet et al., 1999). The amount of MCPA released after one desorption step, expressed as a percentage of the amount sorbed (P_{des}), is given in Tab. 2 for all the soils used.

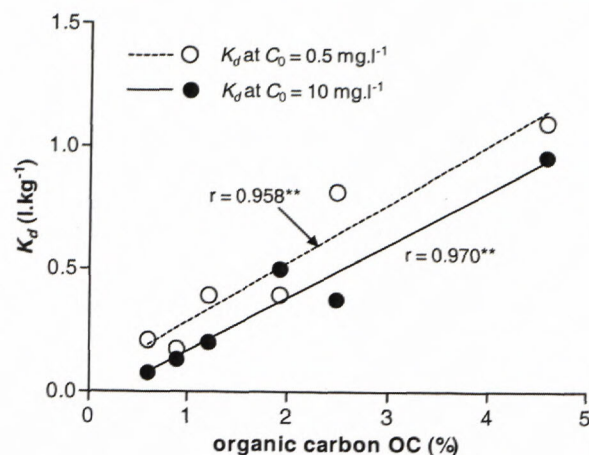


Fig. 1. Relationship between distribution coefficient (K_d) and soil organic carbon content for weak acid herbicide MCPA. ** $P < 0.01$ – significant at the 99 % probability level.

The largest parts of MCPA (the low K_{des} values and high P_{des}) were released from soils with the low organic carbon contents and very low MCPA sorption, as indicated by the K_d values (Tab. 2). Conversely, only about 10–20 % of the originally sorbed amounts of MCPA (the high K_{des} values) were released from soils with the relatively high organic carbon contents and MCPA sorption (Tab. 2). The experimental results show that the release of MCPA from soils is affected by the soil organic carbon content and the percentage of MCPA released is inversely proportional to the organic carbon content (Fig. 2). The relationship between desorption and soil organic carbon content was confirmed by the significant correlations found between OC (%) and K_{des} at both MCPA initial concentrations, 0.5 and 10 mg.l^{-1} (Fig. 2). The decrease in MCPA desorption with the increase in the soil organic carbon content could be due to the restricted diffusion of the herbicide within soil micropores during desorption (Rodríguez-Cruz et al., 2004). Previous studies reported a great importance of soil organic matter for MCPA desorption with the amounts of MCPA released ranging between 15 and 100 % of the sorbed amount in the soils (Sørensen et al., 2006; Thorstensen et al., 2001a). Moreover, it appears that binding strength of MCPA sorption by soils increased when organic carbon content was elevated as the amount of MCPA desorbed was lower in the soil samples with higher organic carbon content (Tab. 2). Thorstensen et al. (2001a) reported that sorption and desorption were inversely correlated for dichlorprop, MCPA and propiconazole in the soils from Norway.

3.2. Estimation of leaching potential

To predict leaching potential of herbicides into groundwater, the groundwater ubiquity score (GUS) (Gustafson, 1989) is often used. It is calculated using the following relationship: $\text{GUS} = \log t_{1/2}(4 - \log K_{OC})$, where GUS represents a dimensionless index, $t_{1/2}$ (d) is the herbicide half-life in soil representing a herbicide persistence and K_{OC} (l.kg^{-1}) is the sorption coefficient

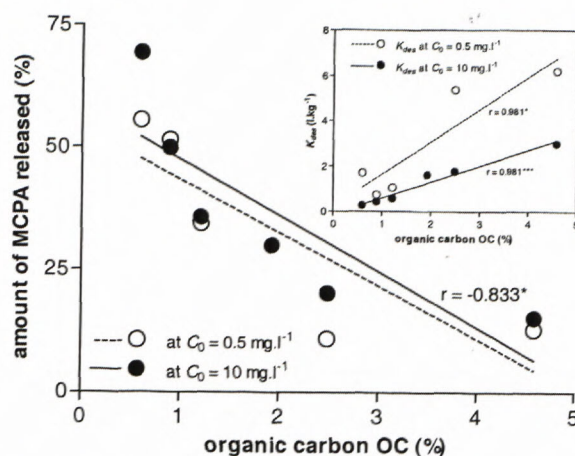


Fig. 2. Relationship between the percentage of MCPA released or desorption coefficient (K_{des}) and soil organic carbon content. *** $P < 0.001$ and * $P < 0.05$ – significant at the 99.9 % and 95 % probability level, respectively.

corrected for soil organic carbon content. Herbicides with $\text{GUS} < 1.8$ are ranked as non-leachers, whereas herbicides with $\text{GUS} > 2.8$ are leachers, and hence will likely contaminate groundwater. Those with GUS between 1.8–2.8 are considered transitional. To calculate GUS for MCPA in all the surface soil samples, the measured organic carbon distribution coefficients (K_{OC} ; Tab. 2) and average half-life (12.67 d) estimated from Crespin et al. (2001), Müller and Buser (1997), Thorstensen et al. (2001b) and Tomlin (2001) were used. The calculated GUS values are presented in Fig. 3.

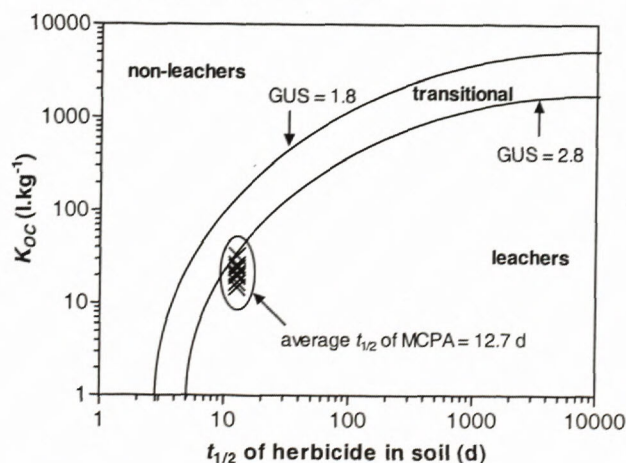


Fig. 3. Prediction of the MCPA leaching potential from the organic carbon distribution coefficients (K_{OC}) determined for the surface soil samples (A1-5) and average half-life ($t_{1/2}$) estimated from literature data. MCPA in all the surface soils used is considered to represent a groundwater contamination risk because all points (crosslets) are within an area labeled as leachers.

On the basis of GUS criteria could be concluded that MCPA represents relatively high leaching potential into groundwater in all five soils as the calculated GUS are higher than 2.8 or approximately equal to 2.8 (Fig. 3). Haberhauer et al. (2002) and Socías-Vicianá et al. (1999) demonstrated that MCPA moved easily with the water front in soil columns with more than 70 % and 99 % of

the herbicide collected in the leachate, respectively. Sørensen et al. (2006) investigated sorption-desorption processes and biodegradation of MCPA in two soil profiles and confirmed the high mobility of this herbicide, especially in the deeper parts of the soil profile containing low amounts of soil organic carbon. The high mobility was caused by the low amount of MCPA sorbed to the soils, as well as by the absence of its biological decomposition. Very little or no degradation of MCPA in the deeper parts of soils and aquifers observed by Harrison et al. (1998) and Sørensen et al. (2006) indicate that, if vertical movement of soil solution brings MCPA to the deeper parts of soil profile, the leaching potential and risk of groundwater contamination may be even higher than suggested by the simple analysis presented in our study. The high water solubility of MCPA, its low sorption in the soils with low organic carbon content observed in this study (Tab. 2), as well as in the studies of Sørensen et al. (2006) and Thorstensen et al. (2001a), easy leachability of MCPA in soil columns (Haberhauer et al. 2002; Sociás-Vicianá et al. 1999) might potentially result in undesirable occurrence of the herbicide in groundwater, and hence it potentially represents an enhanced threat to human health.

4. Conclusions

The retention of MCPA by representative soils seemed to be primarily controlled by the soil organic carbon content. The low distribution coefficient values of MCPA indicate that this herbicide is potentially mobile in all the soils evaluated. The low retention of MCPA by soils was probably a result of the high soil pH. The release of MCPA was influenced by the soil organic carbon content. A significant linear correlation coefficients exist between the percentages of MCPA released or desorption coefficients and the soil OC content. Desorption appeared to be the result of a complex, time dependent interplay of several chemical and physical processes, leading to hysteresis.

To estimate leaching potential of MCPA into groundwater, the measured K_{OC} values as well as average degradation half-life taken from literature were used. The calculated values of groundwater ubiquity score imply that MCPA is the mobile herbicide in all the soils used and has relatively high leaching potential into groundwater. This is very important from an aspect of human health protection.

Acknowledgements

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Environmental and health risk assessment maps: Application of geochemical survey data

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Abstract. Through the combination of methodological approaches of risk analyses with methodological approaches of geochemical mapping, a new way of cartographic depiction and quantitative evaluation of the environmental and health risk level has been created to assess the risk from main compounds of the geological environment of the Slovak Republic. In addition to the Republic's level, the assessment of the main administrative and regional units of the Slovak Republic (districts, municipalities, catchments, and geomorphologic units) in both map and numerical form is also presented.

The calculation of environmental risk is based on comparison of PEC (Predicted Environmental Concentration) with PNEC (Predicted Non Effect Concentration) concentrations of the most significant contaminants – especially potentially toxic elements in groundwater, soils and stream sediments. Health risk – expressed either in the form of excess lifetime carcinogenic risk affections or as a chronic risk Hazard Quotient ($HQ = ADD/RfD$) was calculated for groundwater and soils. Performed calculations are transformed into maps on the level of total Slovak territory (areal distribution) or maps of administrative (districts, municipalities) and regional units (catchments, geomorphological units) based on the expression of the average risk for the evaluated entities.

Key words: geoenvironment contamination, potential toxic elements, environmental risk, health risk, Slovakia

1. Introduction

Since the 1980s the approach in environmental contamination assessment has been shifted from descriptive forms towards evaluation of probable adverse impacts upon other environmental compartments and human health. Terms like *environmental*, *ecological* and *health risk* have been defined and adopted and methodological procedures and legislative directives for their risk assessment have been elaborated.

Combining methods of risk analyses and results and methodological proceeding of geochemical mapping a concept of numeric evaluation and map visualization of potential environmental and health risk from contamination of geological components of the environment was elaborated. Presented work proceeds from national geochemical databases of Slovak Republic acquired within the frame of the programme of Geochemical Atlas of Slovak Republic in the scale 1 : 1 000 000 (Vrana et al., 1997) and environmental-geochemical mapping of selected regions in the scale 1 : 50 000 (Rapant et al., 1999). In the presented work, there are summarized some examples of geochemical data elaboration and utilization at national as well as regional level (Rapant, 2002; Rapant & Kordík, 2003; Rapant et al., 2003; Rapant, 2005; Rapant & Krčmová, 2006).

2. Environmental risk

In the terms of the valid Slovak (Anon, 1998) and European (Anon, 1994) methodological approaches and directives for risk assessment and management the

following definition has been adopted: Environmental risk (ER), is defined as characterizes likelihood, or occurrence possibility of adverse effects as a consequence of the environment exposure to single or several stressors. For single stressor (contaminant) it represents the ratio between its concentration within environment - Predicted environmental concentration (PEC) and concentration with presumed no negative effect upon organisms or ecological systems - Predicted non-effect concentration (PNEC). Consequently, the environmental risk can be expressed numerically by the environmental risk quotient (Q_{ER}). Its magnitude determines the occurrence probability of ill-effects of the assessed contaminant upon environment. Geochemical data, at the sufficient sampling density, in the form of PEC concentrations are representative enough for large regional scales. The best way to define PNEC value, which does not comprise the probability of environmental ill-effects, is to apply the ecotoxicological monitoring methods. The PNEC or NOAEL (No Observed Adverse Effect Level) determination of concentrations of single elements at regional scale for various types of the environment, various geological matrixes and various toxic pollutant combinations is very difficult. The regional scale is the simplest way to apply the limit concentrations from valid environmental and technical standards as PNEC concentrations. For instance in the case of groundwater there is possible to use limit values for drinking water and for soils and sediments reference "A" values of permissible indicants of contamination (so-called Dutch Lists). These values represent natural background content values valid for a non-contaminated environment. Recently, they have also been derived from

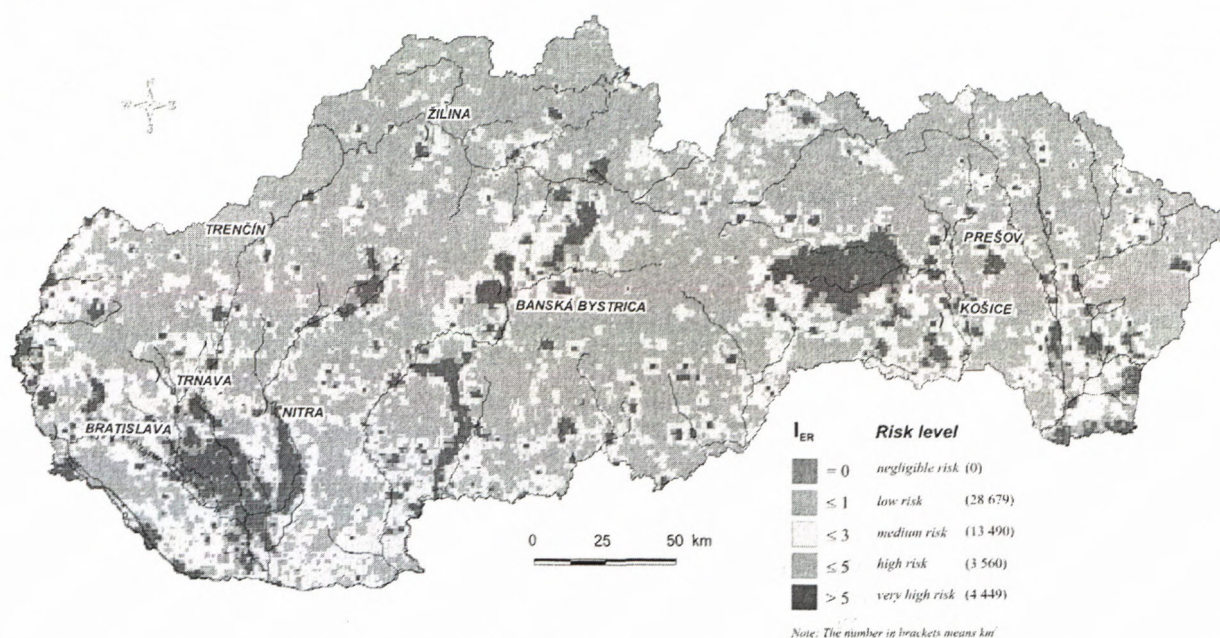


Fig. 1. Environmental risk assessment map of Slovak Republic.

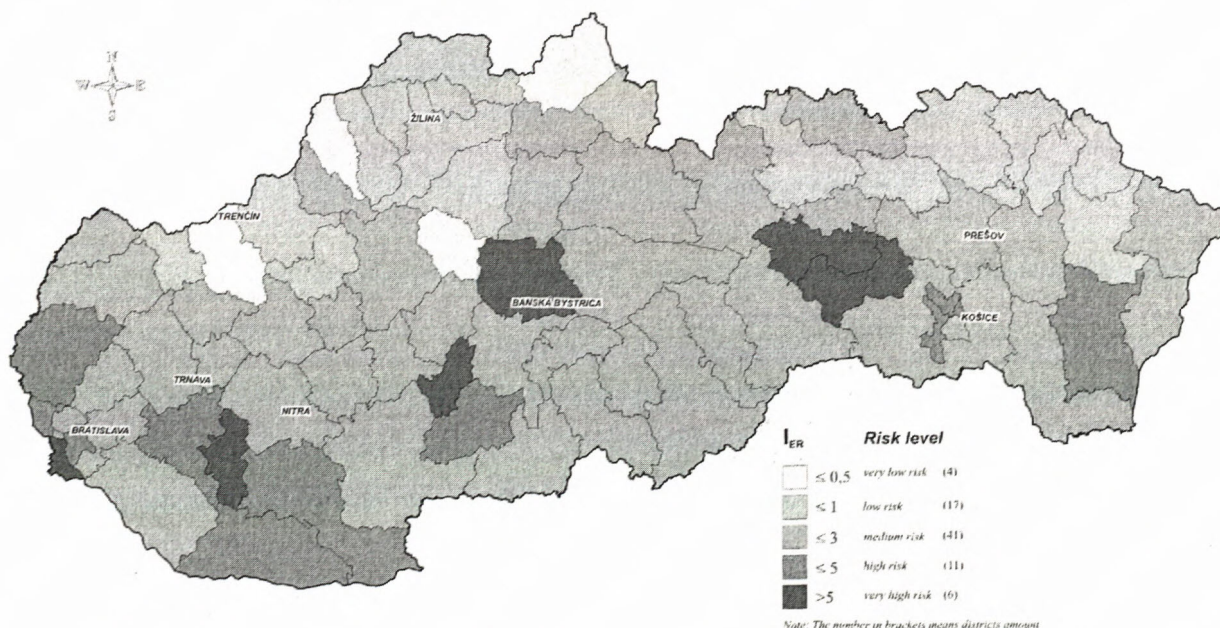


Fig. 2. Environmental risk assessment map of Slovak republic – districts.

toxicological effects of individual elements. In this case, the environmental risk quotient (Q_{ER}) represents the ratio between analytical and limit (risk) concentration values. The summary effect of several elements, in which analytical concentration values in more than one case exceed the limit values, is possible to express in form of the risk sum of individual elements by the environmental risk index (I_{ER}). Those elements, which analytical concentration levels are below their limit (risk) concentration values, have to be excluded from calculation. The environmental risk index value (I_{ER}) calculation for individual analysed water, soil and sediment samples consists of two steps. The first step is the calculation of the environmental risk quotient for each analysed chemical element/compound, which exceeds the limit risk values. In the

second step, their sum is calculated according to the denoted scheme:

$$I_{ER} = \sum_{i=1}^n Q_{ERi} \quad Q_{ERi} = \frac{AC_i}{RC_i} - 1$$

Q_{ERi} – environmental risk quotient of the i -element, which exceeds the risk (limit) concentration;

AC_i – i -element analytical concentration; RC_i – i -element risk (limit) concentration;

I_{ER} – environmental risk index of the sample tested.

Those contaminants, which concentration do not exceeds the limit (risk) values and, consequently they do not pose any environmental risk (ER), ought to be ignored in the calculation (their $Q_{ER} = 0$). In this way, through determination of I_{ER} for each evaluated environ-

Tab. 1. Environmental risk from contamination of geological compartments of the Slovak Republic – districts

	District	I_{ER}	$I_{ER_{gw}}$	I_{ER_s}	$I_{ER_{ss}}$		District	I_{ER}	$I_{ER_{gw}}$	I_{ER_s}	$I_{ER_{ss}}$
1	Spišská Nová Ves	12.81	1.41	16.60	20.41	37	Vranov nad Topľou	1.35	2.30	0.44	1.30
2	Gelnica	12.74	2.38	23.59	12.24	38	Trnava	1.27	2.88	0.09	0.84
3	Šaľa	6.18	15.08	0.20	3.25	39	Detva	1.25	0.57	0.48	2.70
4	Banská Bystrica	5.28	1.58	6.49	7.76	40	Dolný Kubín	1.23	0.84	1.64	1.21
5	Banská Štiavnica	5.22	2.96	3.16	9.55	41	Snina	1.18	2.02	0.47	1.05
6	Galanta	4.99	11.45	0.14	3.37	42	Sobrance	1.17	2.97	0.10	0.44
7	Bratislava	4.04	10.64	0.25	1.23	43	Rimavská Sobota	1.16	2.65	0.27	0.57
8	Krupina	3.49	3.58	0.70	6.18	44	Stará Ľubovňa	1.14	0.56	1.37	1.50
9	Komárno	3.43	9.06	0.11	1.12	45	Brezno	1.11	0.92	1.09	1.31
10	Košice	3.41	3.80	1.32	5.11	46	Poltár	1.09	2.18	0.43	0.67
11	Michalovce	3.16	8.14	0.38	0.95	47	Zlaté Moravce	1.06	1.51	0.24	1.43
12	Nové Zámky	3.14	6.51	0.11	2.81	48	Revúca	1.06	1.85	0.56	0.77
13	Malacky	3.12	7.72	0.28	1.37	49	Topoľčany	1.04	1.81	0.18	1.12
14	Dunajská Streda	2.92	7.39	0.06	1.30	50	Ilava	1.02	0.22	0.60	2.23
15	Liptovský Mikuláš	2.73	5.84	0.93	1.43	51	Poprad	1.00	1.25	0.60	1.15
16	Žarnovica	2.65	2.35	2.08	3.52	52	Žilina	0.99	1.35	0.88	0.74
17	Prievidza	2.63	4.85	0.60	2.45	53	Martin	0.87	0.69	1.10	0.82
18	Trebišov	2.49	6.71	0.25	0.50	54	Humenné	0.83	1.61	0.51	0.37
19	Košice-okolie	2.47	2.43	2.02	2.95	55	Svidník	0.78	1.20	0.45	0.69
20	Prešov	2.32	2.99	0.84	3.12	56	Stropkov	0.78	1.65	0.20	0.48
21	Partizánske	2.30	2.91	0.26	3.72	57	Myjava	0.73	0.66	0.69	0.82
22	Hlohovec	2.26	4.29	0.14	2.33	58	Bardejov	0.71	1.27	0.37	0.50
23	Pezinok	2.10	3.22	0.75	2.32	59	Medzilaborce	0.71	0.68	0.78	0.67
24	Ružomberok	2.07	2.81	2.61	0.78	60	Bytča	0.68	0.87	0.56	0.62
25	Senec	2.05	2.80	0.06	3.30	61	Kežmarok	0.66	0.54	0.75	0.68
26	Žiar nad Hronom	1.97	0.94	2.37	2.61	62	Trenčín	0.65	0.90	0.34	0.71
27	Levice	1.93	3.84	0.25	1.72	63	Sabinov	0.63	0.73	0.70	0.46
28	Skalica	1.92	4.32	0.11	1.33	64	Bánovce nad Bebravou	0.62	1.37	0.15	0.34
29	Senica	1.90	4.83	0.20	0.68	65	Tvrdošín	0.60	0.86	0.41	0.53
30	Veľký Krtíš	1.84	4.60	0.12	0.82	66	Považská Bystrica	0.56	0.73	0.57	0.38
31	Rožňava	1.80	0.79	1.58	3.03	67	Čadca	0.55	0.35	0.41	0.90
32	Piešťany	1.68	3.21	0.34	1.50	68	Kysucké Nové Mesto	0.53	0.69	0.36	0.54
33	Nitra	1.67	3.06	0.06	1.89	69	Turčianske Teplice	0.50	0.28	0.77	0.44
34	Lučenec	1.41	3.15	0.17	0.93	70	Nové Mesto nad Váhom	0.49	0.77	0.34	0.35
35	Levoča	1.40	1.16	1.04	2.00	71	Námestovo	0.48	0.42	0.14	0.87
36	Zvolen	1.37	1.30	0.63	2.19	72	Púchov	0.42	0.29	0.31	0.65

Note: $I_{ER_{gw}}$, I_{ER_s} , $I_{ER_{ss}}$, I_{ER} – environmental risk indexes for groundwater, soils, stream sediments and geological compartments as a whole.

mental sample, we will get the expression of potential cumulative risk from all contaminants, which exceed the limit risk content.

To express I_{ER} spatial distribution within individual geological components – soils, water and stream sediments – it is possible to apply mathematical-statistical approaches, which have been developed for depiction of spatial distribution of chemical elements in single-element maps in the Geochemical Atlas. These are so-called “pixel” maps – maps based on spatial distribution model, which are compiled through averaging and smoothing of primary analytical data.

Based on the above mentioned methods, the indexes of environmental risk were calculated for all samples of groundwater, soils and stream sediments, utilizing the databases of the Geochemical Atlas of Slovak Republic. Consequently, the maps of environmental risk for groundwater, soils and stream sediments were compiled.

Through the unification of the ER maps for individual geological components of the environment, the cumulative

ER map from the geological environment contamination of the Slovak Republic was created (Fig. 1). This summary map was compiled in such a way that for each pixel Environmental risk indexes I_{ER} from soils, groundwater and stream sediments were summarized and averaged.

The comprehensive map provides a complex evaluation of the environmental risk resulting from contaminated geological environment. The environmental risk level was consequently transformed from the maps of whole Slovakia to the respective main regional or administrative units – geomorphological units, catchments, districts (Fig. 2) cadastral units etc. For each of the presented entities a numerical evaluation of environmental risk was also calculated (Tab. 1). Proposed method of calculation and map visualization of environmental risk level enabled to assign the areas with increased environmental risk from contamination of geological environment for the territory of Slovak Republic.

Summarizing the results we can state that more than 57 % of the territory of Slovak Republic belong

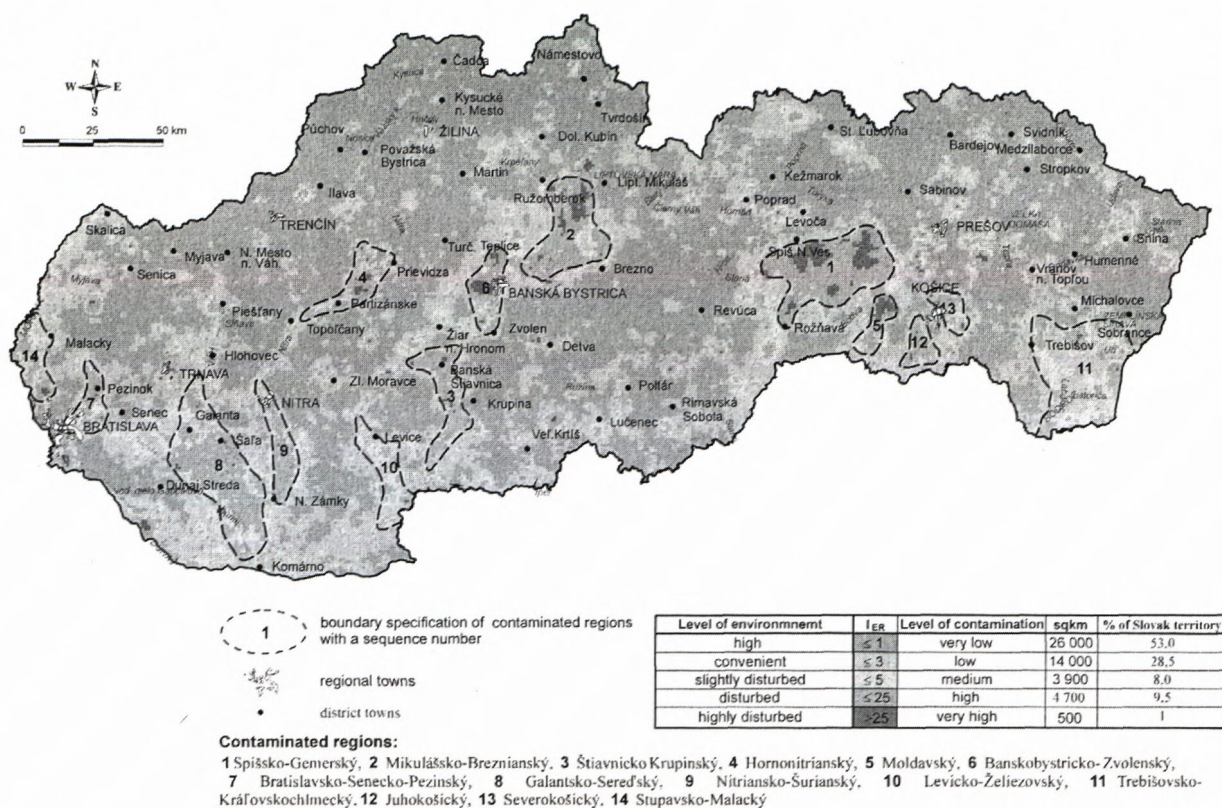


Fig. 3. Environmental-geochemical regionalization of Slovakia.

Tab. 2. Basic characteristics of contaminated regions of Slovakia

CONTAMINATED REGIONS	area sqkm	I _{ER}	THE MOST SIGNIFICANT CONTAMINANTS			LEVEL OF CONTAMINATION		
			groundwater	soils	stream sediments	ground-water	soils	stream sediments
1. Spišsko-Gemerský	910	20.7	As, Sb, Fe, Mn	Hg, Sb, As	Cu, As, Hg, Pb, Sb	++	++++	++++
2. Mikulášsko-Breznianský	650	14.5	As, Sb, SO ₄	As, Sb, Cu	As, Sb, Cu, Hg	+++	++++	++++
3. Štiavnicko-Krupinský	400	9.0	Fe, Mn, SO ₄ , NO ₃	Pb, Cu, Mo	Cd, Cu, Zn	++	+++	++++
4. Hornonitrianský	320	8.1	As, Fe, Mn, NO ₃	Hg, As	As, Hg	+++	+	+++
5. Moldavský	150	20.3	Mn, NO ₃ , Fe	Ni, Cr, Sb, As	Sb, Ni, Cu	++	+++	++++
6. Banskobystricko-Zvolenský	280	13.8	Sb, Cd, As	Cu, Sb, Hg	Cu, Hg	+	+++	++++
7. Bratislavsko-Senecko-Pezinský	220	7.1	NO ₃ , SO ₄ , Fe, Mn	Ba, Sb, Cu	Sb, As, Cu, Hg	+++	+	+++
8. Galantsko-Sereďský	1 100	6.9	NO ₃ , SO ₄ , Mn, Fe	Ni, Cu	Hg, Cu, Cd, Zn, Cr	++++	+	++
9. Nitriansko-Šurianský	290	7.0	NO ₃ , Mn, NH ₄ , Fe	Mo, Ba	Hg, Cd, Cr	++++	+	++++
10. Levicko-Želiezovský	350	4.3	NO ₃ , Mn, Fe	Cu, Sb, Hg	Zn, Cu, Hg	++++	+	++
11. Trebišovsko-Kráľovsko-čhlmecký	1 100	4.3	NO ₃ , TDS, Cl, Mn	Ni, Cu, Cr	Cu, Pb, Se, Ni	++++	+	+
12. Juhokošický	150	8.2	NO ₃ , Mn	Sb, As, Ni	Sb, As, Cd	++	++	++++
13. Severokošický	140	6.5	Mn, Fe, NO ₃	Cu, Sb, Hg	Cu, Ba	+++	++	+
14. Stupavsko-Malacký	300	6.8	Fe, Mn, NO ₃ , SO ₄	Hg, Ni	Hg, Sb, Zn, Cu	++++	+	++

Note: level of contamination: +++++ very high, +++ high, ++ medium, + low

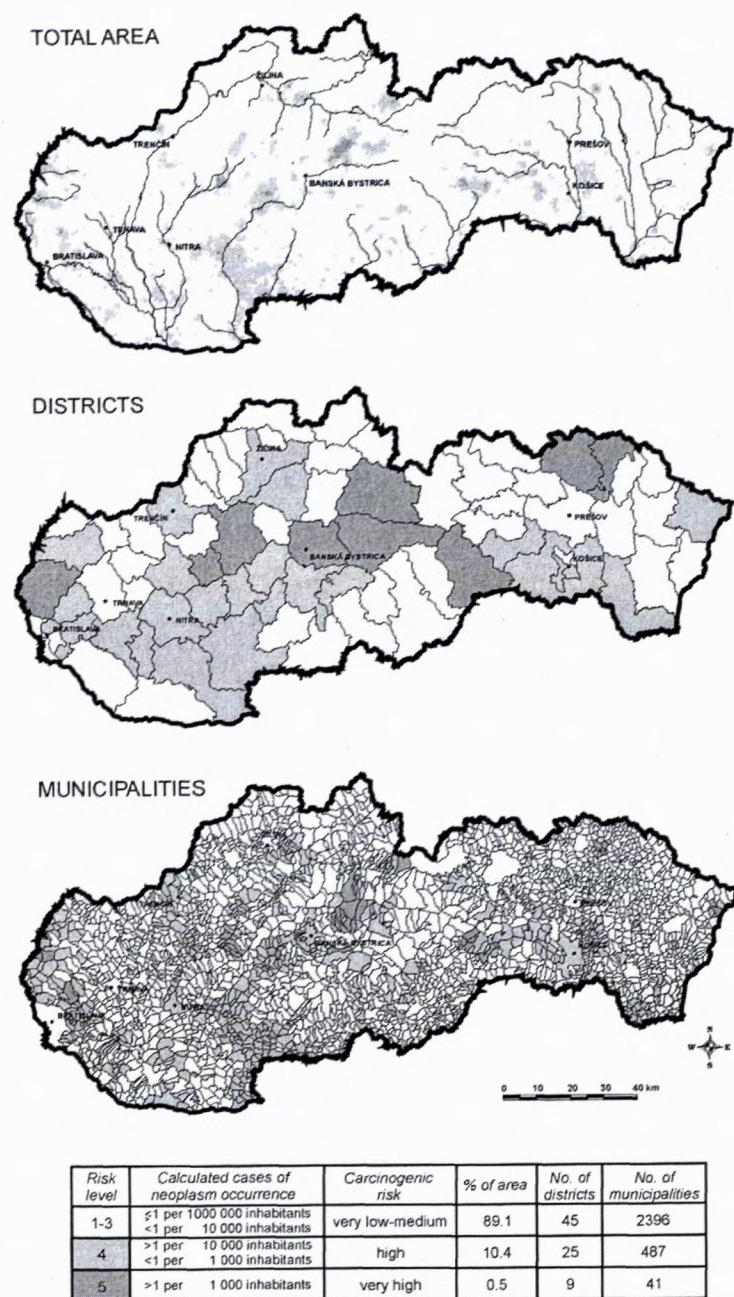


Fig. 4. Risk level maps of carcinogenic affection occurrence from arsenic groundwater contamination in Slovakia.

to category of low – negligible risk ($I_{ER} < 1$). Very high environmental risk ($I_{ER} > 5$) from the contamination of geological compounds of the environment occurs approximately in 9 % of the total area of Slovakia.

Based on calculations and spatial synthesis of environmental risk index [I_{ER}] distribution a territory of Slovak Republic was from the point of view of geological environment contamination (groundwater, soils and stream sediments) divided into 5 basic environment quality levels: high [53 % of Slovak territory], convenient [28.5 %], slightly disturbed [8 %], disturbed [9.5 %] and highly disturbed [1 %]. 14 the most significant contaminated regions of Slovakia were determined and characterized in areas with disturbed and highly disturbed environment (Fig. 3, Tab. 2).

3. Health risk

Potential influence of the environmental contamination by toxic elements upon the health status of the population in the Slovak Republic is manifested by calculation of the human health risk. The human health risk was calculated from soils and groundwater (potentially drinking water). The calculations were realized in two ways: US EPA methodic – calculation of lifetime chronic and carcinogenic diseases occurrence (Risk Assessment, 1999) and Hazard Quotient Calculation – $HQ = ADD/RfD$. The calculation supposed 70 years exposure duration, 70 kg body weight and intake by ingestion. The mean groundwater ingestion rate was estimated at 2 l per day. Soil ingestion rate for children was 100 mg/day and for adults 50 mg/day. Exposure duration (ED) for adults was 64 years and for children 6 years. Lifetime was 70 years. Exposure frequency (EF) expressed as number of days per year was in a case of soils following: for adults 40 days/years (2/7x5/12) and for children 120 days/years (5/7x6/12). As reference doses were used values defined by US EPA (1999). The results of the health risk calculations (carcinogenic and chronic effects) for individual compounds are presented in a map form.

For the carcinogenic risk level assessment (the risk of neoplasm increment) the US EPA 5-steps scale was adopted (on the base of excess lifetime cancer risk affection); (Tab. 3).

The chronic risk level was assessed also in the terms of US EPA (1999) using 4-steps assessment scale according to the ratio magnitude ADD/RfD (Tab. 4).

At the HQ of non-carcinogenic risk, the value $HQ > 1$ is assumed as a risk presence.

From the health risk level maps – chronic and carcinogenic affections result that approximately 0.5 % of the territory of Slovak Republic is characterized with very high cancer risk (above all arsenic, Fig. 4) and 10 % of the Slovak territory comprises the areas with high risk of chronic disease occurrence from potentially toxic elements (As, Sb, Cd, Hg and Pb).

These synoptic health risk assessment maps of total Slovak territory should be considered for only orientation. For the health risk calculations it is necessary to use lower detection limits for analytical determination of chemical elements than those used compiling the geochemical atlases. Proposed methodics were successfully applied within the frame of the pilot project of medicine geology in Slovak Republic (Rapant et al., 2003), in the area of Spišsko-gemerské rudohorie Mts., which represents one of the most contaminated areas of Slovakia, mainly due to mining activities. Based on new sampling, a map of health risk assessment in relation to carcinogenic and chronic disease occurrence within particular municipalities of the region could be realized (Figs. 5 and 6).

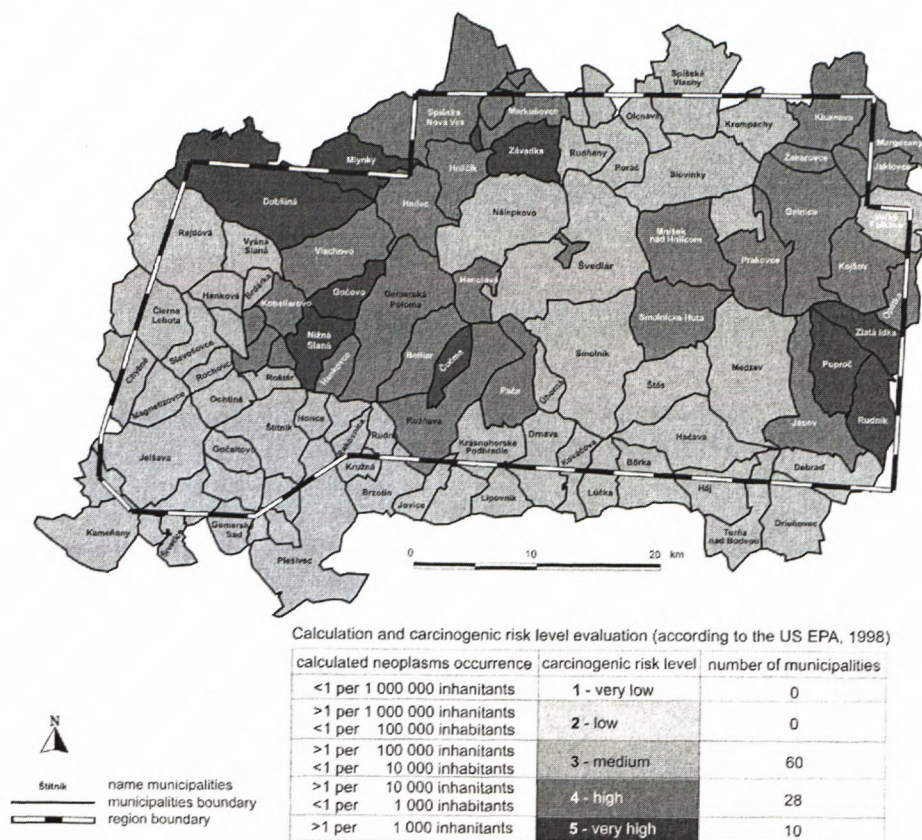


Fig. 5 Risk level map of carcinogenic affections from arsenic – groundwater; SGR Mts., Slovak Republic.

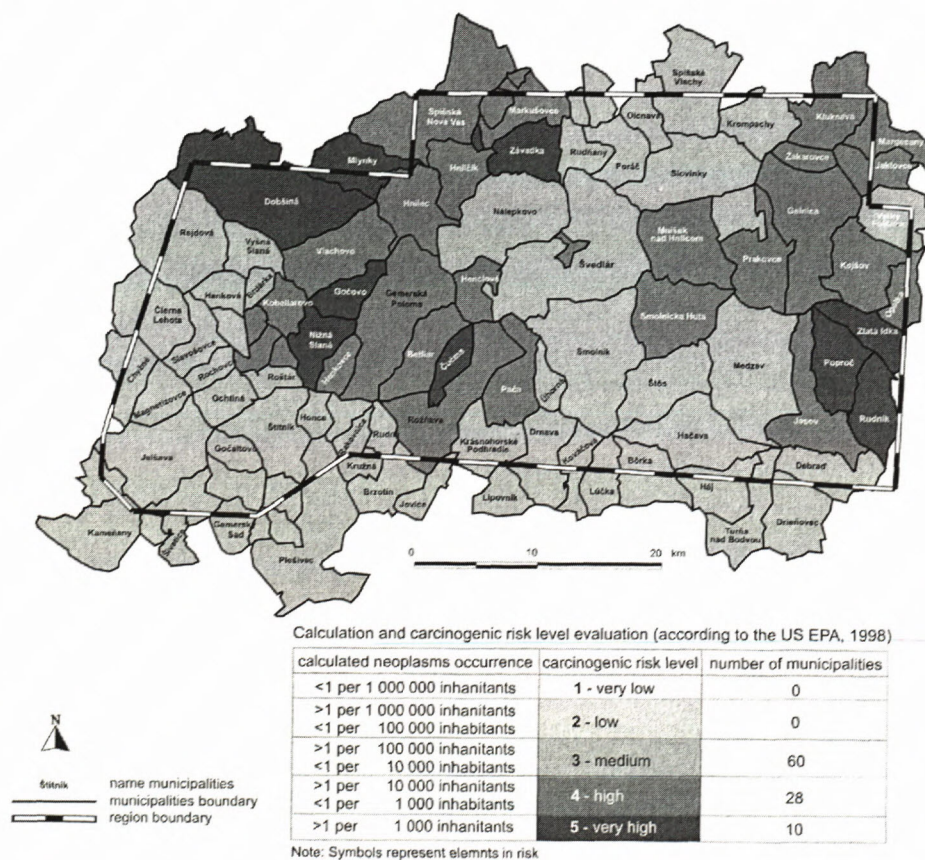


Fig. 6. Risk level map of chronic diseases from potentially toxic elements (As, Ba, Cd, Cr, Hg, Pb, Sb, Se, Zn) children, soils; SGR Mts., Slovak Republic.

Tab. 3 Scale for carcinogenic risk level assessment.

Risk level	Calculated neoplasm occurrence	Neoplasm occurrence risk
1	< 1 per 1 000 000 inhabitants	very low
2	> 1 per 1 000 000 inhabitants < 1 per 100 000 inhabitants	low
3	> 1 per 100 000 inhabitants < 1 per 10 000 inhabitants	medium
4	> 1 per 10 000 inhabitants < 1 per 1 000 inhabitants	high
5	> 1 per 1 000 inhabitants	very high

Tab. 4 Scale for chronic risk level assessment.

Risk level	HQ (ADD/RfD)	Chronic disease occurrence risk
1	≤ 1	no risk
2	$> 1 \leq 5$	low
3	$> 5 \leq 10$	medium
4	> 10	high

4. Conclusion

The proposed method for calculation and visualization of environmental and health risk allows to highlight those areas with enhanced risks. The new methodology for environmental and health risk calculation and visualization presented in this paper provides plenty of possibilities for the efficient application of national geochemical databases and data from geochemical atlases.

From the methodological point of view, the environmental and health risk assessment procedures can also play an important role in the calculation and visualization of environmental stress factors for geological settings.

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Sequence analyses of the Smolník creek stream sediments contaminated by acid mine drainage from abandoned mine (Western Carpathians, Slovakia)

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Abstract. Abandoned mine area has been taken as a model area to document the metal pollution of soil. The Smolník deposit was definitively closed and flooded in 1990-1994 (Jaško et al., 1996, 1998; Lintnerová 1996; Lintnerová et al., 1999). Acid mine drainage (AMD) generation could be presented as the main risk environmental problem related with this Cu-pyrite deposit. There are lots of other risks, like the mine heaps, works and mill tailing dumps stability related with a rate of infiltration, water saturation of waste and others combined with local hydrology and climate characteristics. It has been clearly documented, that AMD discharging from the flooded mine acidified and contaminated the Smolník creek with toxic concentration of elements, which have been transported to the river. All mineral and biological parts of the Smolník creek catchment are befallen and suffered due to AMD action. Stream sediments can accumulate metals, As, sulphates and others transported by AMD. Goal of this study is documented impact of AMD onto stream sediments in the vicinity of the creek bank. For stream sediments characterization we used acid dissolution and five-step sequence analyses. We observed a very good correlation between sequence analyses and acid dissolution of stream sediment.

Key words: stream sediments, mine waste, toxic metals, sequence analyses

Introduction

The old mine-district Smolník (in Eastern Slovakia) was definitively abandoned in 1991 and the mine was flooded up. However acid mine water enriched to iron and sulphates, Cu, Zn, As, Al and other elements discharged from underground in 1994 and heavily contaminated the creek water (Jaško et al., 1996; Lintnerová 1996; Lintnerová et al., 1999). Composition and amount of AMD discharged from mine was stabilized and decreased (e.g from TDS: 17 g/l to about 5g/l) from this time nevertheless AMD continually polluted the brook Smolník and river Hnilec water, stream sediments and some surrounding soil (Lintnerová et al., 2006; Rojkovič et al., 2003). Old mining waste dumps, which produce strongly acidic and mineralized AMD, are other serious source of pollution in this area (Tab. 1, Fig. 1). Tailing impoundment producing neutral water with high concentration of metals (especially Fe and As) and salts is the other important source of contamination in this region. All this sources add the contamination directly to the creek Smolník. Contamination is transported in the form of suspended solids (Tab. 2) for a long distance in water of the creek Smolník and river Hnilec and accumulates in stream sediments (Lintnerová et al., 2006).

This work aims to define the accumulation of the mine-derived elements (Cu, Zn, Al, As, Mn) in stream sediments and to characterize their relative mobility and potential bioavailability.

Tab. 1. Sources of contamination in Smolník mine area.

		SM-2	SM-OD	SM-3	SM-5	SM-Kar.
Al	mg/l	82.74	0.187	474	58.6	159.5
Fe (tot.)	mg/l	542.4	4.61	3229	321	1091
Fe (II+)	mg/l	356.8	1.81	421	166	222
Mn	mg/l	35.48	3.35	25.3	38727	170.5
Ca	mg/l	190.2	44.3	304	160	2538.5
Mg	mg/l	328	36.8	442	101	1003.5
SO ₄	mg/l	3642.4	253.75	14800	2220	9057.5
Zn	mg/l	9599	45	43000	7070	24405
Pb	mg/l	81.2	<4	156	18	42.5
As	mg/l	108.4	45.75	16800	140	13

(SM-2 – AMD from shaft Pech, SM-OD – water from tailing impoundment channel, SM-3 and SM-5 – AMD from old waste dump drainage channel, SM-Kar – AMD from mine Karitas; Rojkovič et al., 2003).

Tab. 2. Average chemical composition of suspended solids in Smolník brook and Hnilec river waste (Rojkovič et al., 2003).

		SM-1	SM-4	SM-6	SM-8	H-0	H-1
Fe	%	5.26	12.99	16.34	17.61	8.43	14.6
Al	%	1.96	7.96	8.68	6.36	3.71	3.76
As	mg/kg	112	142	251	135	124	103
Pb	mg/kg	196	171	163	166	150	106
Zn	mg/kg	1026	512	798	1235	1079	1979
Cu	mg/kg	592	1818	2157	2407	665	1856
Mg	mg/kg	6854	6261	4812	4738	18089	4778
Ca	mg/kg	16990	9531	12217	5306	33924	19101
K	mg/kg	11662	2638	1938	2366	8613	5942
Na	mg/kg	7997	2759	2755	2136	9549	8582
Mn	mg/kg	2536	940	769	819	5379	1439
number of samples		2	3	4	4	2	3

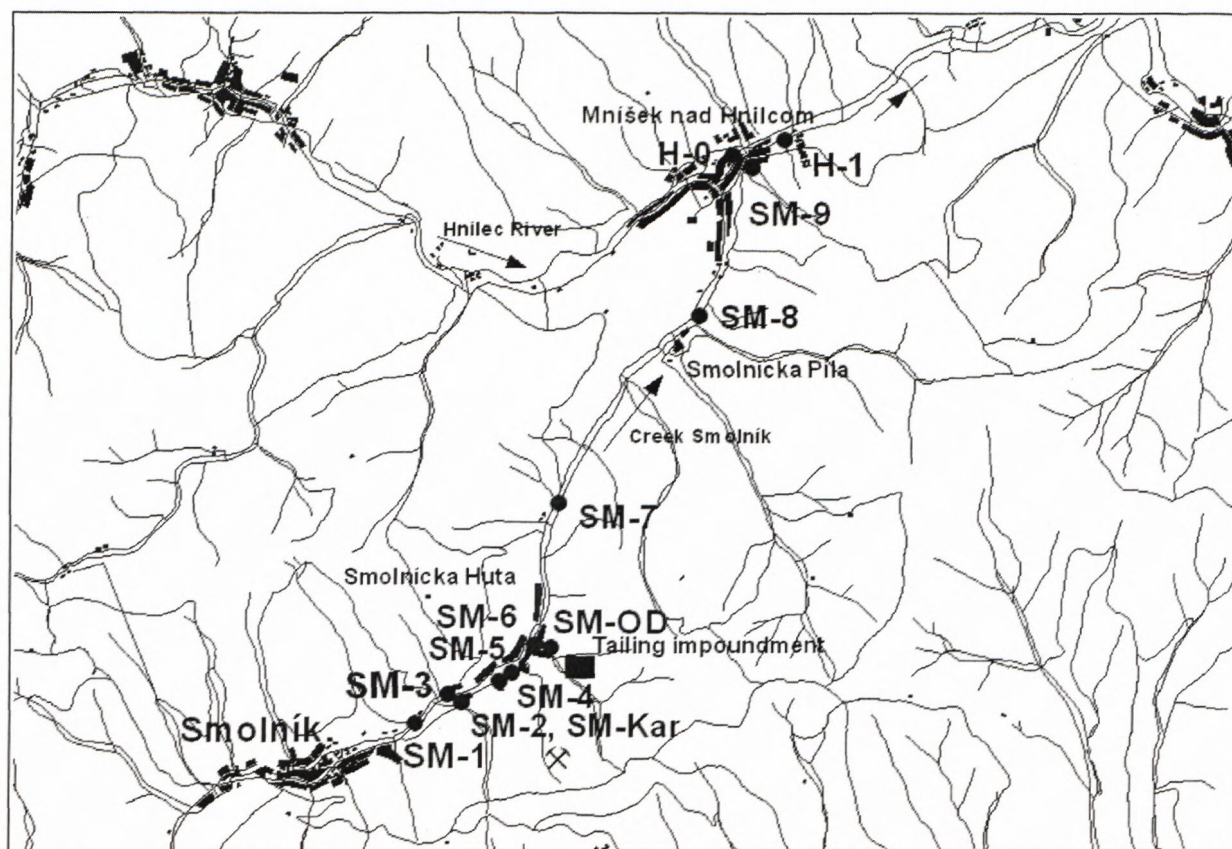


Fig. 1. Fe, As and Cu 5-step sequence analyses of stream sediment from Smolník stream. 1 - extraction in water, 2 - ion - exchangeable and carbonate phases, 3 - reducible – Fe and Mn oxide, 4 - oxidizable – organic mater, sulphides, 5 - aluminosilicate residue.

Methods

Eight samples of stream sediments were collected in June 2002 (Fig. 1). Samples of stream sediments were collected in the vicinity of the water monitoring sites. Sediments were dried (60 °C) and sieved on a < 1 mm screen. Part of homogenized sample was used to measure pH (active, exchangeable), Eh and conductivity in the soil paste. Active pH was measured in mixture of 5 g sample and 25 ml of distilled water and exchangeable pH in mixture of 5 g soils and 25 ml of 1M KCl. Exchangeable Al was determined in 1M KCl extract. 2 g of sample were mixed with 20 ml of 1M KCl and agitated 2 hours. Al was determined photometrically (MERC SQ300) in the filtrate. Water dissolved sulphates were analysed by the same device 1 g of fine sample was extracted 1 hour using the horizontal shaker. Sulphates were measured in filtrate.

Chemical analyses

Metals content (Fe, Mn, Al, Cu, Zn, Na, K, Ca, Mg, Pb, As) in stream sediments were determined by digestion of samples in concentrated HNO₃ for 2 hours at 85 °C. Insoluble residuum was dried at 105 °C and weighted. AAS and ICP AES methods were used to measure elemental concentrations. Concentrated nitric acid extracted all potentially mobile metals in suspended

solids or sediments. This method practically could supply the total analysis of sample (Pontér et al., 1992; Rhoton et al., 2002 and other).

Sequence extraction

Partitioning of metals among various geochemical phases is particularly interesting to assess mobility and ecotoxicity of metals in the catchment area. We used next sequence extraction scheme, developed in the Slovak GS laboratory (Mackových et al., 2003) on the basis of published schemes (Tessier et al., 1979; Rapin and Forstner, 1983; Rapin et al., 1986; Quevauviller et al., 1994). Five samples of stream sediments (SM1, SM4, SM7, SM8 and SM9) were selected and consequently extracted according this procedure. Seven elements - Fe, Si, Al, Cu, Zn, Mn and As were determined in the extracts.

Fraction 1: Extraction in water – inorganic salts, 1g of sample + 50 ml of distilled water, extraction/agitation – 16 hours, centrifugation, metals in supernatant were determined

Fraction 2: Ion - exchangeable and carbonate phases: residue from F1 + 40 ml 0,11M acetic acid (HOAc) 16 hours extraction/agitation, centrifugation – supernatant, metals determination.

Fraction 3: reducible – Fe and Mn oxide: residue from F2 + 40 ml 0.1 M NH₄OH HCl in 25 % HOAc, pH 2, 16

extraction, occasional agitation, centrifugation, metals determination in supernatant.

Fraction 4: oxidizable – organic mater, sulphides: residue from F3 + 2 x 10 ml 30 % H_2O_2 + HNO_3 , 85 °C, 50 ml NH_4OAc - extraction 16 hours, centrifugation, metals in supernatant.

Fraction 5: aluminosilicate residue: residue from F4 + HNO_3 + HF + HClO_4 .

Additional total chemical decomposition (HNO_3 + HF + HClO_4) of sediment samples and analyses of the same metals were performed to verify accuracy of analytical procedure. To compare accuracy of analyses the standard of river sediment CRM 601 (BCR) was used. AAS method with hydride generation was used for determination of As. Cu, Mn, Zn, Al, Fe were determined by ICP AES and Si was analysed by gravimetric method.

Results and discussion

Parameters of stream sediments are closely related to chemistry of stream water, but are not identical. The first step in our study was a basic characterization of stream sediments (Tab. 3). Stream sediment taken close from the place where AMD discharged from the mine (SM-4), directly to the stream Smolník, has low pH. High concentration of sulphide, iron and aluminium is typical for this sediment strongly affected with AMD. The pH of other stream sediments is significantly higher in the lower part of the stream. Higher acidity and content of sulphates were determined in pore solution of the sediment than in fluent water (Tab. 3).

Tab. 3. Basic characterization of stream sediments.

	SM-1	SM-4	SM-7	SM-8	SM-9
pH(water)	6.95	3.23	6.24	5.12	6.58
pH(KCl)	6.59	3.05	5.73	4.86	6.28
Eh	240	390	-150	190	-147
Al (mg/kg)KCl	1.12	228	1.2	2.48	0.8
$\text{SO}_4(\text{v H}_2\text{O})$	800	3550	650	1650	850
Fe (v H_2O)	0	154	12	3.5	7
TOC (%)	1.52	3.02	7.35	4.57	6.95

Negative value of Eh in the lower part of the stream (close to the Smolník stream and Hnilec river confluence) is very interesting especially by potential remobilization of metals adsorbed on Fe oxyhydroxides (samples SM-7 and SM-9). This fact should be supported by the higher concentration of organic matter in stream sediment from this part of the stream.

In the next step of the study we focused on decomposition of stream sediment in HNO_3 . This methodology was used to determine total concentration of available and mobile studied metals. We observed continuous accumulation of Fe in lower parts of the stream (Tab. 4). This phenomenon was found even though the amount of insoluble residuum was higher in this part of the stream. This fact indicates that percentage of Fe oxyhydroxides in soluble part of sediment is rising. High amount of Fe oxyhydroxides is transported in suspended solids and

sedimented in parts of stream with lower kinetic energy of flow (especially in monitoring point SM-8). Aluminium is evidently bounded on aluminosilicate minerals and tailing impoundment is a source of K and Ca.

Tab. 4. Dissolution of stream sediments in HNO_3 (in ppm, IR – insoluble residuum).

Element	SM-1	SM-4	SM-7	SM-8	SM-9
Fe	40800	49600	50800	122800	94800
Mn	676	254	612	484	552
Al	10540	10200	12540	11960	12080
Cu	348	308	254	308	356
Zn	226	130.2	228	184.2	54.8
Na	296	298	268	202	197.6
K	1514	1724	2434	1308	1554
Ca	87.6	32.2	123.8	51.8	234
Mg	6820	5940	4820	4420	4380
Pb	94	66	68	90	12
As	54.4	75.8	46.4	50	53.2
IR (%)	24.16	23.4	30.54	42.76	40

A sequence analysis of stream sediment was used to characterize the amount of metals bound in different phases. Sequential extraction procedures are connected with some problems, mainly partial selectivity, re-adsorption and release of metal during extraction steps, etc. The sufficient information about mineralogical and geochemical nature of stream sediments could eliminate these potential complications. It is well known that mobility of potentially toxic metals depends on their different binding or specific chemical forms and total concentration of metals is not the most important. Metal partitioning in all phases is very important in the case exchangeable or bioavailable phases to assess mobility and environmental risk.

The largest part of studied metals is bounded or adsorbed by oxides and by organic matter. The contents of exchangeable Fe, Cu, Zn, Mn increase mainly in the acidic condition in the sediments. Acid conditions and increased content of organic matter are two important factors, which change the mobility and bioavailability of metals. The most acid sediment is leached (SM-4) and the metals (Mn, Cu, Zn) content decreases. Leaching stops in the point SM-7 vicinity and the largest concentration of metals is in the point SM-8. The SM-7 sample is enriched in organic matter (TOC 7.35 % in comparison with SM-1: 3.5 %), and it could change redox condition and metal mobility in water and the ability of iron oxyhydroxides to attenuate metals.

Significant amount of Si and Al is bound on insoluble residuum (IR); (Tab. 5.). These results correlate with results obtained from acid dissolution of stream sediments. Ratio of Al content in IR and in available phases (sum of phases 1-4) is stable in the whole stream. On the other hand we can observe continuous rising of Al content in available phases downstream the Smolník stream. In samples taken above the mine the percentage of Al adsorbed on oxyhydroxides is only 1 % of total amount, in the lower part of stream about 7 %. It is caused by precipitation and sedimentation of Al in form of oxyhydroxides minerals.

Different situation we can observe in content of Fe. In part of the stream above the mine approximately 85 % of

Tab. 5. Sequence analyses of stream sediments in ppm (5 – insoluble residuum, 1-4 – sum of first 4 steps, available phases, Tot. – total amounts of studied elements).

Tot.	Fe	Al	Si	Mn	Cu	Zn	As
SM 1	61000	76500	297900	880	377	259	51.4
SM 4	69400	70000	292000	360	333	163	40.9
SM 7	72000	76600	240900	840	277	265	50.2
SM 8	139400	63300	230300	550	318	207	68.3
SM 9	122400	69000	217100	664	400	292	70.9
sum 1-4	Fe	Al	Si	Mn	Cu	Zn	As
SM 1	10440	3760	2921	529	274	158	11
SM 4	17750	6600	2000	38	243	69	9
SM 7	28230	8920	4300	603	237	193	12
SM 8	53790	8060	2824	296	236	105	1
SM 9	31110	10190	9800	415	343	198	1
5	Fe	Al	Si	Mn	Cu	Zn	As
SM 1	50560	72740	294979	351	103	101	40.7
SM 4	51650	63400	290000	322	90	94	32.3
SM 7	43770	67680	236600	237	40	72	38.4
SM 8	85610	55240	227460	254	82	102	66.9
SM 9	91290	58810	207300	249	57	94	69.5

Fe is bound on IR (stable aluminosilicate minerals), and 15 % is adsorbed on available phases (principally on oxyhydroxides Fe – 13 %); (Fig. 2). Rising of Fe oxyhydroxides in stream sediments we can observe in lower part of stream. Percentage of oxyhydroxides in stream sediment represented 31% in the sample SM-8 taken approximately 15 km from the mine (Fig. 1, Fig. 2). It is important if we know that in this part of stream are more reduced conditions in sediments (Tab. 3). The kinetic energy of flow is decreased in this part of the stream due to morphological condition and there are convenient conditions for sedimentation of suspended solids. This fact document increased ratio of Fe amount in available phases and in IR.

For contents of Zn, Cu and Mn there is typical, that amount of these elements adsorbed on available phases (phases 1-4) is higher than the amount bound on IR (Fig. 2). Binding of Cu on sulphides mineral phases (38-48 %) and oxyhydroxides (16-28 %) is dominant phenomena in stream sediments from Smolník stream. Only 25 % (in average) of Cu is bound on stable mineral forms (IR). Similar behavior we can indicate for Zn. Amount of Zn bound on IR is little bit higher (31-51 %), and main part of Zn is adsorbed on oxyhydroxides

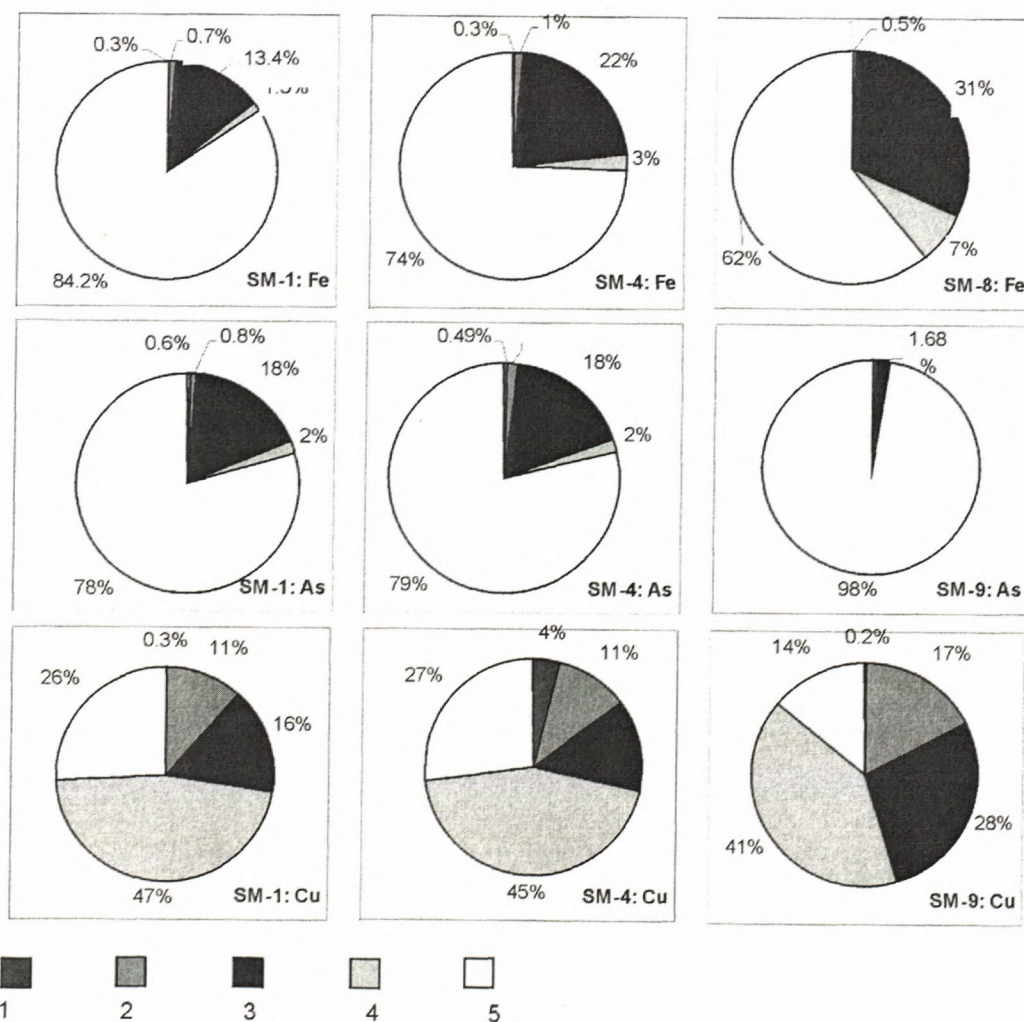


Fig. 2. Correlation of Fe and Cu in samples analysed by acid dissolution (HNO_3) and sequence analyses (SNV).

Explanatory notes: The content of elements in: 1 – water, 2 – exchangeable, 3 – reducible, 4 – oxidizable 5 – residual fractions.

(20-26 %) and on ion - exchangeable and carbonate phases (16-36 %). Amount of Zn occurred in oxidisable phases (organic matter and sulphides) represent 13-19 %.

Different results we obtained for As (Fig. 2). In samples taken close the mine and tailing impoundment we detected increased content of As adsorbed on oxyhydroxides (18-19 % from total amount of As in stream sediment). We can document that tailing impoundment is an important source of As in this area. Concentration of As in available phases is higher in sample SM-7 taken below the tailing impoundment, than in sample SM-4, taken below the mine. In the last two samples taken close to the confluence of Smolník stream with Hnilec river the whole As is bounded on residual mineral phases. This fact documents that Fe-oxyhydroxides precipitates with As are not transported in the form of suspended solids by stream.

If we compare results of sequence analyses and HNO_3 acid dissolution of stream sediments (Fig. 3) we can observed good correlation between these two methods, mainly for Fe, Cu, Zn and Mn. Values obtained by acid dissolution are little bit lower than total amount of studied elements obtained by sequence analyses. It is understandable, because acid dissolution by HNO_3 is not total dissolution, and some stable mineral forms stay in insoluble residuum. On the other hand, content of elements obtained by acid dissolution of stream sediments is little bit higher then content of elements from available phases obtained by sequence analyses. It is caused by partial dissolution of aluminosilicates by HNO_3 . This result indicates that for quick and rough characterization of stream there sediments is possible to use acid dissolution for determination of available amount of some

elements. Predictably for exact results and characterization of different phases is necessary to use sequence analyses.

For characterization of changes of stream sediments from Smolník stream we can use comparison of our results with results from 1996 (Jaško et al., 1996) realized by HNO_3 dissolution too (Fig. 3). The content of studied elements is approximately the same nowadays than 10 years ago; especially if we know that the samples were not taken from exactly identical places.

Conclusions

- mine derived contamination is transported in dissolved form and in suspended solids in the Smolník stream catchment
- contents of Fe, Cu and Zn in stream sediments continuously increase downstream the Smolník stream
- tailing impoundment is a permanent source of As contamination
- 30 % of Fe in the form of oxyhydroxides is in stream sediments
- HNO_3 extractions of stream sediments correlated with sequence analyses

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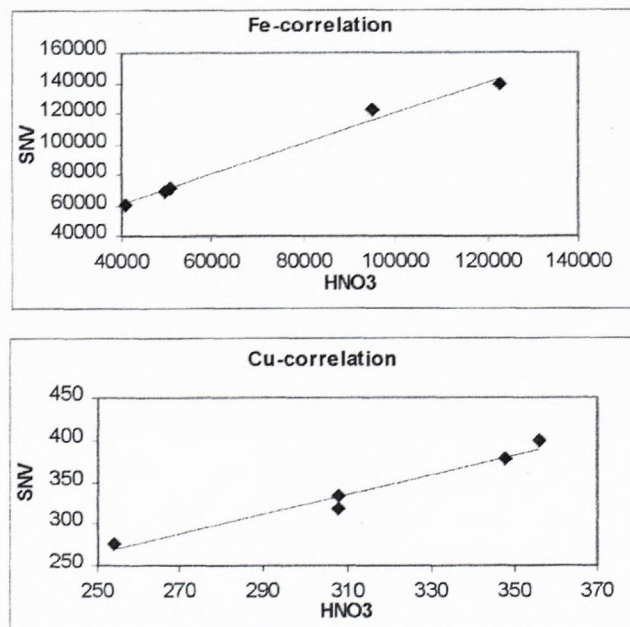


Fig. 3. Comparison of Fe and Cu amount extracted from stream sediments by different methods upper HNO_3 - acid dissolution (Tab. 4), SNV - sequence analyses total, lower SNV - sequence analyses available phases 1-4 (Tab. 5), 1995 - acid dissolution from Jaško et al., 1996).

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Geochemical study of arsenic mobility in secondarily influenced Kyjov brook and Ondava river (Eastern Slovakia)

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Abstract. This study describes arsenic distribution and its mobility in surface waters and stream sediments of watersheds of the Kyjov brook and partly the Ondava river, localized in Eastern Slovakia. Study area is characterized by the intensive contamination of surface waters and stream sediments with a high concentration of arsenic. It is obvious that the arsenic originates from impoundment located in the upper part of the Kyjov catchment. The impoundment operated by local chemical factory consists of waste from chemical industry and burning waste. Extreme concentrations of arsenic were found in the vicinity of impoundment: 11,39 mg.l⁻¹ in the sample taken from surface water in June 2000 and 3208 mg.kg⁻¹ in the sample collected from stream sediment in June 2005. We assume that the release of arsenic from the waste material highly depends on snow melting or higher precipitation events. Contamination of surface waters with arsenic is large-scaled and it extends more than 50 km downstream the Kyjov brook and the Ondava river. This observation suggests serious environmental load with potential negative influence on aquatic environment and human health. On the ground of these findings, a comprehensive research of different compartments of environment is highly requested.

Key words: arsenic, geochemistry, surface water, contamination, impoundment, stream sediments

1. Introduction

Arsenic is a chemical element with natural occurrence in the environment. Interest in the study of arsenic in the aquatic environment has been increased in very recent years. Arsenic belongs among the most important contaminants in the environment with the wide-range potential risk to human health. Arsenic can occur in the environment in several oxidation states (+5, +3, 0, -3), but in natural waters is mostly found in inorganic form as ox anions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. The most important factors controlling arsenic speciation are red ox potential (Eh) and pH. Organic As forms can be produced by biological activity, mostly in surface waters, but they may mainly occur in waters significantly impacted by industrial pollution (Smedley & Kinniburgh, 2002). The metal oxides, mainly Al, Fe and Mn oxides are the major minerals significantly binding arsenic (dissolved As forms, arsenate and arsenite; Sullivan and Aller, 1996). Therefore Al, Fe oxides can importantly limit the mobility of arsenic in aquatic environment. It has been observed that Ca-carbonates can also affect retention of arsenates by soils and stream sediments (Hiller, 2003). Microorganisms including microscopic fungi are capable to transform inorganic arsenic forms to various inorganic and organic volatile and nonvolatile arsenic compounds (Ševc and Čerňanský, 2003).

Arsenic accumulation in the environment is due to both natural and anthropogenic sources. Increased arsenic concentration (higher than 50 µg.l⁻¹) can occur in vol-

canic sedimentary rocks or in geothermal areas (Rapant et al., 1996; Nimick et al., 1998). Anthropogenic sources of arsenic are mainly caused by activities such as combustion of fossil fuels, mining and smelting of ores, agricultural uses of arsenical pesticides or releasing from wastes deposited on spoil heaps and impoundments (Ďurža and Khun, 2002). By the weathering of waste material from mining activity (which contents arsenopyrite FeAsS) anomalous arsenic concentrations in natural waters can be observed, locally reaching up to thousands of µg of arsenic (e.g. Loredó et al., 2003 – range 4100–5600 µg.l⁻¹ of As).

Toxicity of arsenic and its potential risky influence on human health is one of the chief topics of many scientific works. In recent years this topic has been related to high contamination of drinking water supplies in the West Bengal (Das et al., 1996), in Bangladesh (Smith et al., 2000) and other countries (Urminská et al., 2004; Rapant and Krčmová, 2006). Long-term overexposure to As can cause skin, liver, bladder, kidney and lung cancers and many other health effects (ATSDR, 1989; Wu et al., 1989; Jain and Ali, 2000).

Arsenic distribution and its mobility in surface waters and stream sediments of watersheds of the Kyjov brook and partly the Ondava river is presented in this paper. Pollution of aquatic environment by arsenic in the study region (Eastern Slovakia) was observed in the late 1990s for the first time (Kordík and Slaninka, 2001). Arsenic comes from impoundment located in the upper part of the Kyjov catchment near the Poša village (Fig. 1). The impoundment operated by local chemical factory consists of waste from chemical industry and

burning waste. During the first research, extremely high concentrations of arsenic were found in the surface water in the vicinity of impoundment with maximum value of 11.39 mg.l^{-1} in the sample from June 2000 (Kordík and Slaninka, 2001). In 2005, a comprehensive research was started in the contaminated area to obtain more information on arsenic distribution in various compartments of the environment and to define the actual extent of arsenic contamination.

The main objectives of this paper are following:

- identification of spatial pattern of arsenic contamination in surface waters and description of its trends,
- comparison of arsenic contents in surface waters with water quality guidelines,
- synthesis and interpretation of new information and allocation of potential risk and impact of contamination to natural equilibrium in the aquatic environment.

The research results will create the information base for representatives of decision makers (Ministries) as well as local authorities. The knowledge obtained during the scientific activities should lead to the final implementation of a strategy focused on reduction of the negative impact of contamination in the area. Information will support the water management system by many important issues such as identification of contamination "hot spots" etc. that requires relevant scientific data and information.

2. Methods

2.1 Sampling, laboratory techniques and data sources

Geochemical research for presented part of study includes sampling and subsequent analysis of surface water. Regarding water-sample collection, the used data are based on a criterion of ecological objective, e.g. sampling sites are situated in the areas with expected natural background concentrations of analysed parameters as well as in the contaminated part of the study area.

Water samples were received from the following data sources:

- Geochemical atlas of Slovakia – part Groundwater for description and calculation of referenced condition (Rapant et al., 1996),
- National monitoring program of surface water quality realized by SHMI (SHMI Annual report on surface water quality),
- Research related to study of geological factors of environment – TIBREG region (Kordík and Slaninka, 2001),
- Research realized in 2005.

Water samples were collected into the PVC bottles and stabilized by 5 ml of concentrated HNO_3 . The water samples were analysed in a hydrochemical laboratory of INGEO Inc. Žilina and ŠGÚDŠ Bratislava. A review of analytical technique and detection limits applied to arsenic (also for stream sediments) is given in Tab. 1. The accuracy of analytical data was continuously assured by the system of analytical quality assurance (AQA) corresponding to the European standards. The polysulphone vacuum filtration instrument NALGENE (USA) and nitrocellulose membrane filters SYNPOR with $0.45 \mu\text{m}$ pores were used

in membrane filtration (samples collected in 2005 and samples used from Geochemical atlas).

All data are stored in the database programme MS Access and used in GIS.

Tab. 1. Laboratory parameters for determination of arsenic in water and stream sediment.

Element	Detection limit		Method
	INGEO Žilina	ŠGÚDŠ Bratislava	INGEO Žilina, ŠGÚDŠ Bratislava
As	0.001 mg.l^{-1}	0.0001 mg.l^{-1}	AAS-HG – Atomic Absorption Spectrometry - Hydrid Generating

2.2 Data processing

The distribution of arsenic, determination of environmentally significant concentrations as well as the background and critical values are discussed in the paper. Several approaches to process the data gained from the research are used:

- application of statistical analysis,
- comparison of the results with a baseline or background distribution given in Rapant et al. (1996) and Kordík and Slaninka (2001),
- comparison of the results with legislative standards (legislative approach).

Basic statistics is a standard method used for assessment of analytical results. Arithmetic mean, median, standard deviation, minimum and maximum values of analysed components are the parameters applied to describe the central tendency and variability of element distribution in waters (Tab. 4). Moreover the individual contents of arsenic are presented as well (Tab. 2).

The legislative approach is based on comparison of observed concentrations with the limit values that are given as a standard and defined for particular components of the geologic environment. To evaluate the content of contaminants in waters, Decree of Slovak Health Ministry No. 151/2004 on drinking water demands and drinking water quality control and Slovak Technical Standard (STN 75 7221) were used for the of comparison. This legislation strictly limits arsenic contents in waters (Tab. 2).

Interpretation of the results is supported by graphical visualization providing comprehensive information about arsenic distribution in the study region.

3. Results

Based on the results from regional research of environmental geological factors (Kordík & Slaninka, 2001) and the results of long-time monitoring of surface waters performed by the Slovak Hydrometeorological Institute (SHMI), a large-scale contamination of the Kyjov catchment by highly toxic element – arsenic was observed. Furthermore, the high values of total dissolved solids (TDS), ammonium ions, sulphates and nitrates in surface water were determined in studied area. High arsenic concentrations (much higher than a background value) were observed also in the Ondava river into which the Kyjov

Tab. 2. Concentrations of arsenic in the Kyjov brook and the Ondava River and important values of arsenic content in waters (all values in $\mu\text{g}\cdot\text{l}^{-1}$).

Sample No.	Sampling date							
	05/1999	07/1999	06/2000	07/2002	01/2003	07/2003	01/2004	08/2004
109 (Ondava)	12.59	10.00	5.4	11	113	17	-	3.1
112 (Ondava)	-	0.26	-	-	-		-	-
113 (Ondava)	-	77.60	-	-	-		-	-
122 (Kyjov)	10667	-	11385	2870	7000	3460	1932	2208
129 (Kyjov)	-	6700	-	-	-		-	-
131 (Kyjov)	-	7150	-	-	-		-	-
Regional background mean value for surface water	According to data given in Kordík & Slaninka, 2001 2.6							
Geochemical atlas – groundwater (Rapant et al., 1996)	Arithmetic mean 1.9				Median 0.5			
Drinking water standard	According to decree of Slovak Health Ministry No. 151/2004 10							
Surface water standards (STN 75 7221)	I. class 10	II. class 20		III. class 50		IV. class 100		V. class > 100

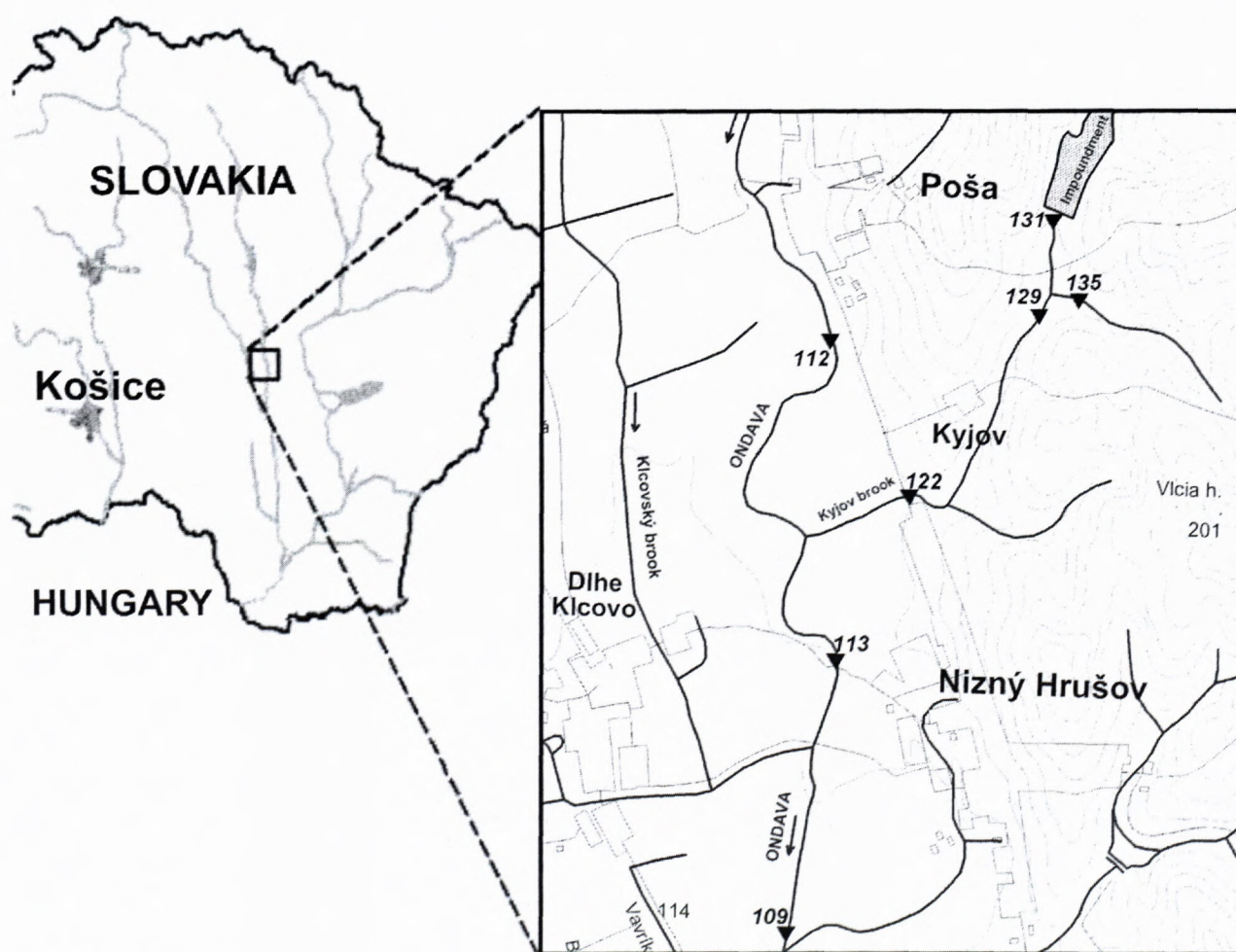


Fig. 1. Schematic map of the study area and sampling sites of the surface water during the period 1995 – 2004.

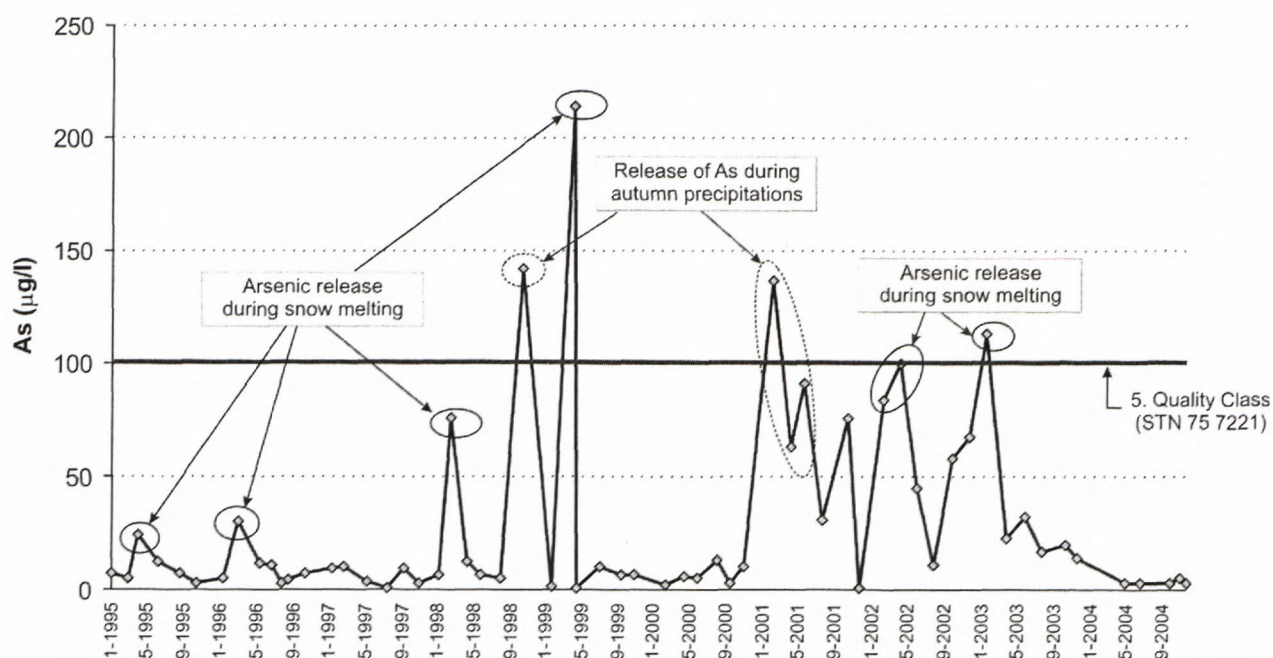


Fig. 2. Seasonal variation of As concentration in the Ondava river during 1995 – 2004 (SHMI sampling site No. 109 near the Nižný Hrušov village – SHMI, 1995-2004).

brook inflows nearby the village of Nižný Hrušov. The investigated area and the sampling points of the surface waters are presented in Fig. 1.

The source of As contamination in the study region is put down to an impoundment located in the upper part of the Kyjov catchment. Impoundment was built in 1977 and was designed for depositing the burning waste and waste from burning coal (Pivovaráčiová et al., 1989). The founder and owner of the impoundment is chemical concern, with production targetted at basic products of organic and inorganic chemistry – benzene chemistry, productions of cyclohexane, cyclohexanol, manufacture of industrial fertilizers, products based on ammonia, manufacture of concentrated nitric acid for nitration purposes and other (Annual Report, 2004)

Selected analytical results of arsenic contents of the sampled Kyjov brook and the Ondava river are presented in Tab. 2 (period 1999 – 2004). The quality of surface water in the Ondava river (sampling site Nižný Hrušov – No. 109) is permanently monitored by the Slovak Hydrometeorological Institute. Geological Survey of Slovak Republic regularly monitors sampling site No. 122 (located at the border of Nižný Hrušov village). Other sampling sites represent one-shot measures taken during the study of geological factors of the environment in the "TIBREG" region in 1999 (Kordík and Slaninka, 2001). Moreover, a background mean value of arsenic and limit concentrations valid for drinking waters and surface water quality are given in Tab. 2 in order to compare significant values of arsenic with the measured arsenic contents in the area.

Sampling point No. 112 (Ondava river – located upstream to the confluence with the Kyjov brook) shows very low As concentration ($0.26 \mu\text{g.l}^{-1}$), typical for back-

ground natural conditions in the area. Much higher arsenic contents have been observed in the contaminated part of the Ondava river located downstream to the confluence with the Kyjov brook (up to $113 \mu\text{g.l}^{-1}$). Extreme values of arsenic are characteristic for the whole Kyjov catchment (reach the values in thousands $\mu\text{g.l}^{-1}$).

Concentrations of arsenic in groundwaters of Slovakia range from $0.5 \mu\text{g.l}^{-1}$ to $887.5 \mu\text{g.l}^{-1}$, with the mean As concentration only $1.9 \mu\text{g.l}^{-1}$ and median $0.5 \mu\text{g.l}^{-1}$ (Rapant et al., 1996). Arsenic distribution pattern in surface waters of Slovakia is very similar to the groundwaters. Arithmetic mean of As concentration for surface waters of Eastern Slovakia is $2.6 \mu\text{g.l}^{-1}$ with minimum values under the detection limit ($0.5 \mu\text{g.l}^{-1}$) and the highest concentration $118 \mu\text{g.l}^{-1}$ (extreme arsenic concentrations from the Kyjov brook were excluded from the calculation of statistical parameters). Decree of the Slovak Health Ministry No. 151/2004 on drinking water demands and drinking water quality control and Slovak Technical Standard (STN 75 7221) strictly limit the arsenic contents in waters (values are given in Tab. 2). Based on the above mentioned arsenic concentrations and legislative standards it is obvious, that the measured concentrations of As especially in the contaminated Kyjov catchment show very high values. In other words, the arsenic concentrations in the Kyjov brook are app. 20 to 100 times higher in comparison to the arsenic limit value for V. quality class of surface water ($100 \mu\text{g.l}^{-1}$) and app. 2000 to 10000 times higher than the upper permissible value of arsenic for drinking water. In addition, arsenic contents in the contaminated part of the Ondava river (downstream to the confluence with the Kyjov brook) frequently reach values exceeding drinking water standard.

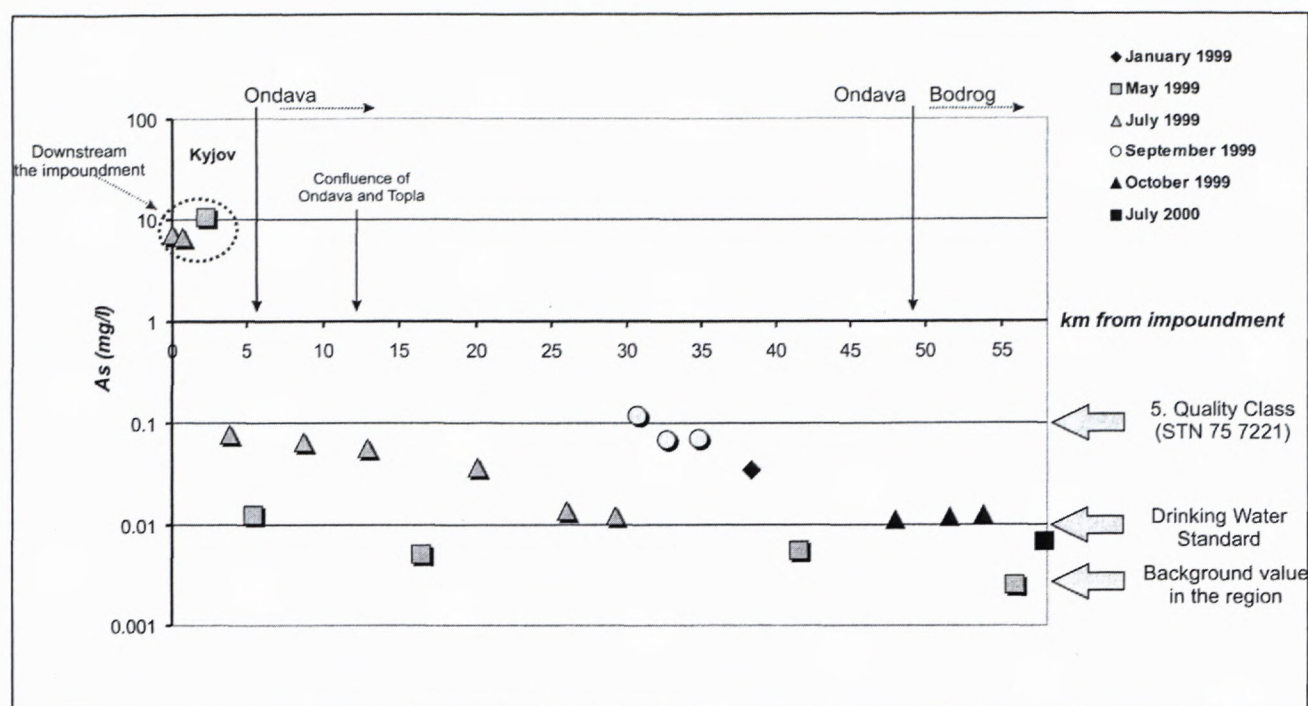


Fig. 3. Profile of arsenic distribution in the Kyjov brook, the Ondava and the Bodrog Rivers.

According to the results, the research of surface waters quality during the period 1995 – 2004 clearly shows very high level of arsenic contamination of the whole Kyjov catchment and partly the Ondava river. These observations suppose an environmental load with potential influence on human health. For instance, epidemiological studies in areas with As concentration ranging from 350 to 1140 $\mu\text{g.l}^{-1}$ in drinking waters reported increased cancer risk (EHIS, 2000). We assume that the large amount of the As from the waste material. Mainly entered technological waters and rainfall in surroundings of impoundment affect the release of As and induce contamination of surface waters and stream sediments in the Kyjov brook and the Ondava river.

Data from the national monitoring programme performed by SHMI display concentration variability of arsenic in surface waters (Fig. 2). Variability of As concentration is obviously influenced also by seasonal conditions. It was found out that snow melting or higher precipitation events have also eminent influence on arsenic contents in surface water. Moreover, seasonal climatic changes could have a serious impact on variability of dissolved As forms as well. Gault et al. (2003) showed a seasonal difference in the dissolved arsenic concentration and its speciations by changing of As(V)/ ΣAs ratio in surface water.

It was found out in the course of the research that contamination of aquatic environment by arsenic is really vast; it reaches up to more than 50 km downstream the Kyjov brook and the Ondava river. Increased arsenic concentration (above background mean value) has been detected also after the Ondava River joins the Latorica river as well as nearby the Slovak-Hungarian border (the Bodrog river). Profile of arsenic distribution in the Kyjov catchment, the Ondava and the Bodrog rivers is given in Fig. 3. Outstanding concentrations of arsenic are typical

of the Kyjov catchment. Although the concentration rate of As is gradually decreasing downstream the Ondava and the Bodrog rivers, at the end of the rivers profile reach still high values.

The territory of Ondava watershed is a very important water supply area consisting of the fluvial sediments of the Ondava river (Hydrogeological region QN-106). This area belongs to large water resources available in Eastern Slovakia with possible total withdrawal 91 l.s^{-1} (Jetel, 2001). Although no strong contamination of this water-bearing aquifer has been observed yet, the problem with arsenic contamination in the Kyjov catchment could pose serious danger to the groundwater quality of potential water supply (groundwater quality can become worse as a result of other potential sources of contamination such as high population density, industry etc.). In the assumption that mean flow rate of the Kyjov brook is 10 l.s^{-1} (no real data at disposal) and mean As content is 1 mg.l^{-1} downwards the impoundment, it is expected that 315 kg of As is released to the aquatic environment of the Ondava river annually (in several mg.l^{-1}).

Significant contamination was observed also in stream sediments (research under the study). For example, concentration of As in sample No. 122 (Kyjov) reached a value of 284 mg.kg^{-1} (August 2004) and concentration of As close to the impoundment was extremely high reaching 3208 mg.kg^{-1} . The stream sediment in the Ondava river monitoring site (Tab. 3) is also significantly contaminated but showing strong variation of arsenic values. All obtained analytical results of arsenic in stream sediments of the study area significantly exceed natural background level of arsenic (average concentration is 8 mg.kg^{-1}) calculated according the data given in (Kordík and Slaninka, 2001) and represent high environmental risk to the environment.

Tab. 3. Concentrations of arsenic in stream sediments from the Ondava River (in mg.kg^{-1}).

Sample No.113	Sampling date							
	06/1996	06/1998	05/1999	06/2000	08/2001	07/2002	07/2003	08/2004
	38.9	16.7	17.4	105.4	101.5	42.3	60.3	11.9

Tab. 4. Statistical parameters of analytical results in surface waters (all data in mg.l^{-1}).

Kyjov brook (n = 6)										
	TDS	Na	K	NH_4	Cl	SO_4	NO_3	PO_4	As	TOC
Mean	1353.18	199.20	37.57	26.15	131.71	307.66	28.97	1.937	1.7781	30.68
Median	1049.33	103.90	35.87	26.14	125.72	250.65	29.07	2.013	0.4587	29.95
St. Dev.	561.23	215.50	5.02	10.55	16.86	127.30	11.77	0.586	2.5129	2.14
Min.	965.46	99.40	33.80	11.11	120.49	231.45	12.40	1.015	0.3935	29.00
Max.	2340.00	584.65	45.90	39.00	161.01	532.50	40.31	2.50	6.70	33.80
Ondava river (n = 10)										
Mean	399.44	19.83	4.18	0.21	20.90	53.42	5.60	0.198	0.0266	5.33
Median	412.85	19.14	3.84	0.24	21.39	51.25	5.58	0.111	0.0088	5.45
St. Dev.	35.44	7.21	0.78	0.16	6.31	7.11	2.51	0.144	0.0297	0.43
Min.	310.00	10.61	3.18	0.00	9.98	45.25	3.01	0.080	0.0022	4.70
Max.	428.00	34.04	5.90	0.44	26.94	69.15	10.32	0.418	0.0776	5.70
Referenced brooks (n = 17)										
Mean	528.29	25.73	4.63	0.73	29.02	47.45	12.93	0.174	0.00097	
Median	535.00	23.69	4.10	0.20	25.33	45.70	8.95	0.107	0.00075	
St. Dev.	108.62	10.99	3.13	2.06	12.37	18.63	11.92	0.156	0.00053	
Min.	297.00	12.27	1.42	0.01	10.62	14.00	0.79	0.061	0.00050	
Max.	747.00	47.74	13.12	8.65	51.16	90.55	37.79	0.666	0.00232	

For the sake of more detailed geochemical study, additional samples of surface waters were collected in June 2005. Situation map of the sampling sites is presented in Fig. 4. Analytical results showed totally different character of chemical distribution between catchment of the Kyjov brook, the Ondava river and the referenced brooks in the region (Tab. 4). Except for arsenic, statistical parameters of the main ions, TDS and TOC are given in Tab. 4.

Significantly higher values of TDS, ammonium ions, sulphates, nitrates, chlorides and arsenic are typical for the secondarily influenced Kyjov brook. It is very interesting that higher values of total organic carbon (TOC) were obtained in surface waters downwards the impoundment. This might point to organic contamination of the Kyjov brook from impoundment material. Comparison of analytical results from filtered and non-filtered water samples is also considered rather important for assessment of arsenic contamination. In 2005, both the filtered and non-filtered water samples were analysed. The results of this comparison showed that majority of arsenic in the study area is presented in soluble forms.

Relation between arsenic concentration and TDS for the different surface waters (Kyjov catchment, the Ondava river, impoundment and referenced brooks) is presented in Fig. 5. The figure shows a different level of the surface water contamination in the study region. In the

referenced brooks low As concentrations up to $2.32 \mu\text{g.l}^{-1}$ and TDS contents ranging app. from 300 to 700 mg.l^{-1} has been observed. In the Ondava river higher As concentrations are typical and depend on the position to the



Fig. 4. Schematic map of samples localization during June, 2005.

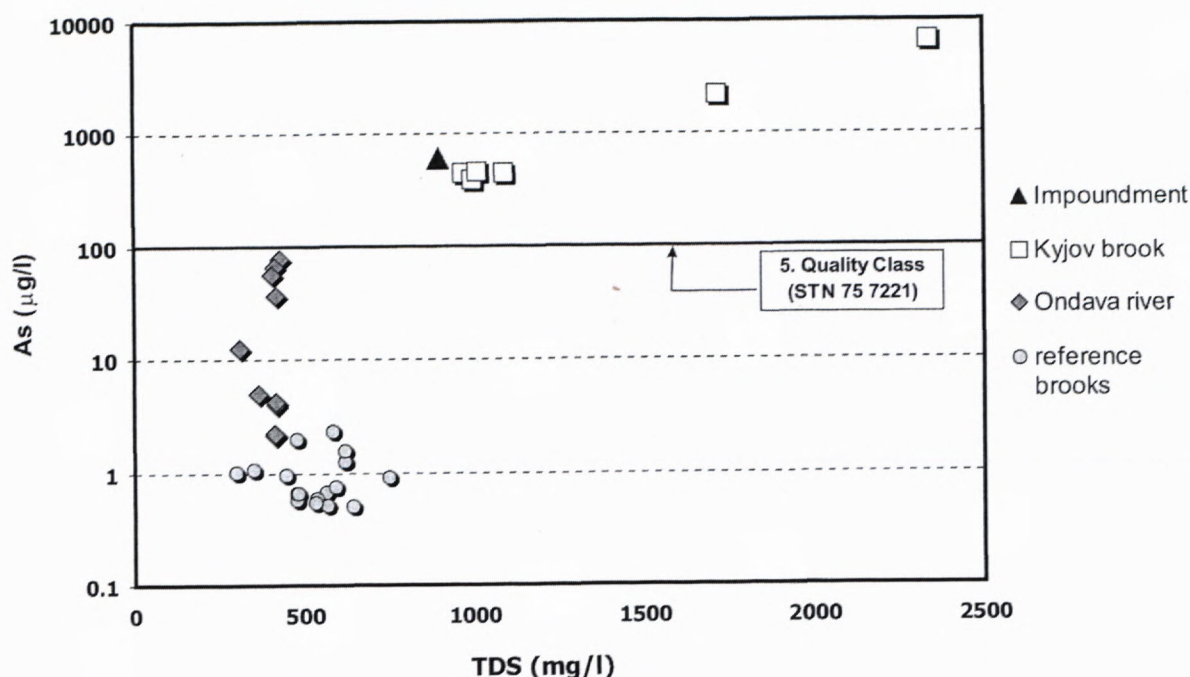


Fig. 5. Distribution and relation of As and TDS in surface waters.

Kyjov brook. The As contents upstream the confluence with the Kyjov brook reach values of about $3\text{--}7\text{ }\mu\text{g.l}^{-1}$ and downstream the confluence of about $10\text{--}100\text{ }\mu\text{g.l}^{-1}$. Contents of TDS are slightly lower than in the referenced brooks (around 400 mg.l^{-1}). Outstanding values of both arsenic and TDS are typical of the Kyjov catchment and impoundment ranging from about 400 to $6700\text{ }\mu\text{g.l}^{-1}$ for arsenic and from about 1000 to 2300 mg.l^{-1} .

4. Conclusions

Basic information about arsenic contamination of aquatic environment in the Kyjov and Ondava catchments (Eastern Slovakia) are presented in the paper. The detailed field research focused on waste material from impoundment, stream sediments and surface waters results in a wide-range arsenic contamination of aquatic environment in the study region.

Significantly higher values of TDS, ammonium ions, sulphates, nitrates, chlorides and especially arsenic are typical of the secondarily influenced Kyjov brook. Increased values of total organic carbon showed organic contamination of the Kyjov brook from impoundment material. Moreover we assume, that large release of As from the waste material is partially influenced also by seasonal conditions (depending on snow melting or higher precipitation events). For risk assessment of As mobility it is important that major amount of arsenic in the locality is present in soluble form.

Significant arsenic contamination is detected also in stream sediments of the Kyjov brook and particularly in the Ondava river (extreme As values downwards the impoundment). This observation supposes serious environmental load with potential negative influence on aquatic environment and human health. In addition, a potential entry of arsenic into the food chain can pose a serious

health risk as well. Increased arsenic values were measured also in biological material from the impoundment, e.g. *Ceratophyllum demersum* 254 mg.kg^{-1} of total As (under the current study). In order to sort out this problem, thorough description and justification of the mobile As-forms, its bioavailability and experimental estimation of sorption and desorption behaviour of As in aquatic environment will be necessary. All obtained field and analytical data should predict the potential risk of arsenic contamination to the water environment.

Acknowledgments

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Assessment of groundwater vulnerability to contamination in the Kampinoski National Park, central Poland

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Abstract: Groundwater vulnerability to contamination in the Kampinoski National Park (KNP) area in central Poland was evaluated as a basis for developing appropriate protection strategy for the groundwater resources and management. The majority of studies have concentrated on detailed investigations in recreation areas located near Warsaw. Assessment was accomplished using U.S. EPA DRASTIC and the travel times to the saturated zone. Results of the study and observations made for a good data base in order to determine the role and value of individual criteria in evaluation of groundwater vulnerability. The final DRASTIC values have been grouped into the medium and medium high natural vulnerability. The travel times to the saturated zone are classified in 11 intervals, ranging from 30 days to 30 years.

1. Introduction

The concept of groundwater vulnerability to contamination is a useful tool for environmental planning, decision-making, protection of the groundwater source and of the groundwater resources. In practice in many countries the new regulations for protection groundwater often supported by groundwater vulnerability and protection zones. Groundwater vulnerability is a concern even in recreation areas such as national parks or landscape parks. Such areas, including Kampinoski National Park in Poland, that they are not isolated from "outside effects", and sometimes outright on the contrary they are a place of constant or temporary by the neighbouring inhabitants.

Kampinoski National Park (area – 385.44 km²) with its buffer zone (area – 385.88 km²) is a UNESCO Biosphere Reserve and it is a special protection area of NATURA 2000 network which plays an essential role in the nature conservation in the EU. KNP is located where four tributaries: the Bug, Narew, Wkra, Bzura rivers, merge with the Vistula river (Fig. 1). According to Ecological System of Protected Areas (ESPA) the valleys of these rivers are ecological corridors. The Vistula river valley in Kampinos forest is especially recognized as an important ecological area in Europe.

KNP is situated within the valley that includes the suburbs of Warsaw, a city of nearly 2 million people. The area is characterized by a diversity of morphology, hydrogeological settings, geology and vegetation as well as infrastructure development.

2. Hydrogeological conditions of KNP region

2.1. Groundwater monitoring network

The monitoring network consists of 56 piezometers and 25 water level gauges (Fig. 2). The spatial distribution of monitoring network measurement points was designed to take full advantage of hydrological and

hydrogeological analysis within an enclosed surface drainage basin and hydrogeological system. The observation points for surface and groundwater monitoring network at KNP have been grouped into seven observational cross sections (Krogulec, 2001, 2004).

The general concept for location of observation points set in Kampinoski National Park local monitoring network was subordinated to meet the following goals:

- Including all existing hydrodynamic zones in observations thus enabling researches to perform full analysis of the diversified water relations in KNP area and its protection zone;
- Including the influence of anthropogenic factors on the chemical composition of groundwater and surface waters;
- Optimizing the number of groundwater and surface water observation points;
- Relating to the existing network and single observation points;
- Providing technical possibility to perform hydrogeological and hydrological observations (easy access, possibility of non-controversial point location etc.).

Measurements of surface and groundwater levels are performed in two weekly intervals from 30. 11. 1998. During the period between 1998-2004 the water table, a fundamental criteria used in evaluation of groundwater vulnerability to contamination, was at depth of 0.61 to 4.7 meters below terrain level. Water table ordinates were at a height of 65.67 to 97.53 (Tab. 1).

2.2. Characteristics of the aquifer

Kampinoski National Park and its buffer zone are located in the central part of the Vistula river valley. This valley flood plains and a river flood terrace (Kampinos Terrace) of the Vistula and Bzura rivers. On the Kampinos Terrace, one aquifer occurs with a thickness of 10 to 50 metres. It is composed of varied, fine-grained

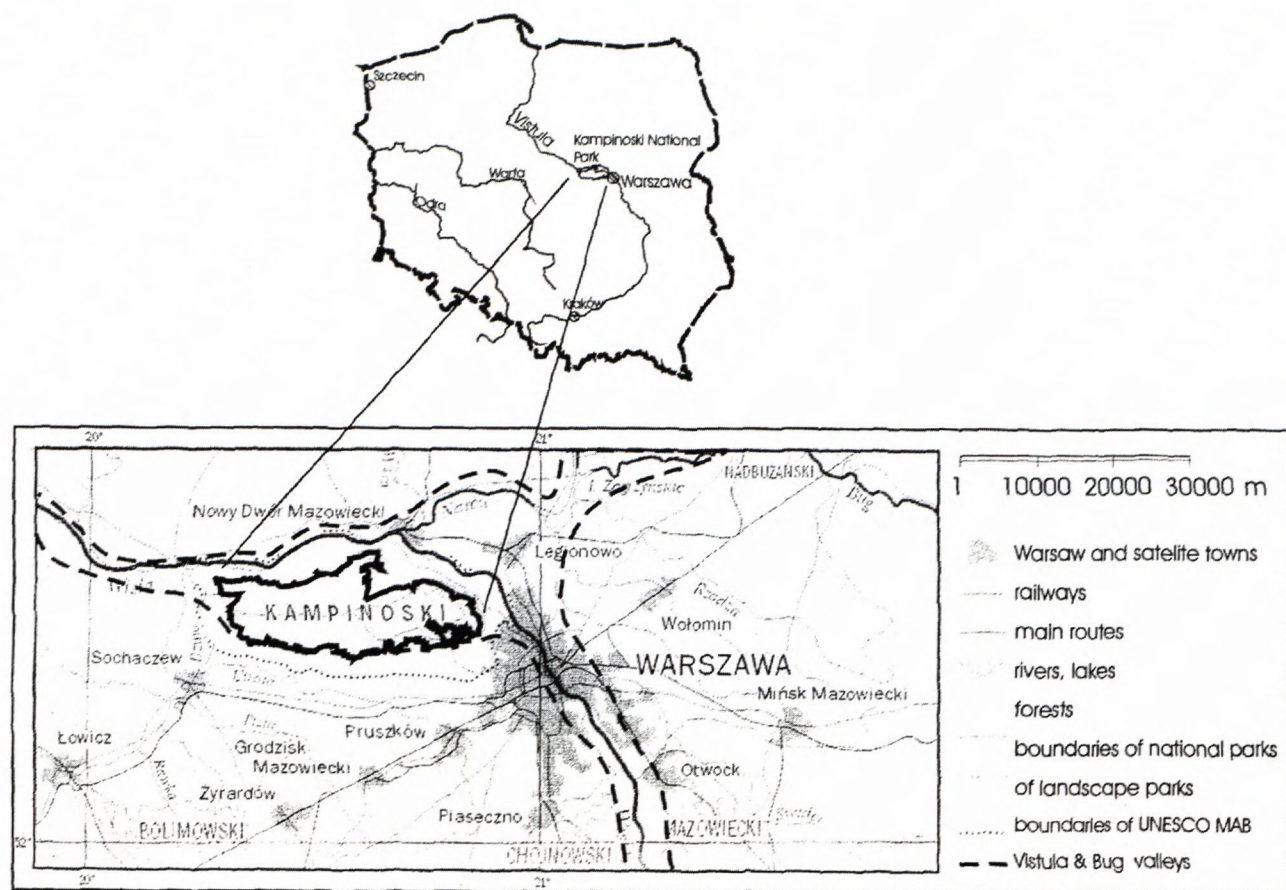


Fig. 1. Location of the Kampinoski National Park.

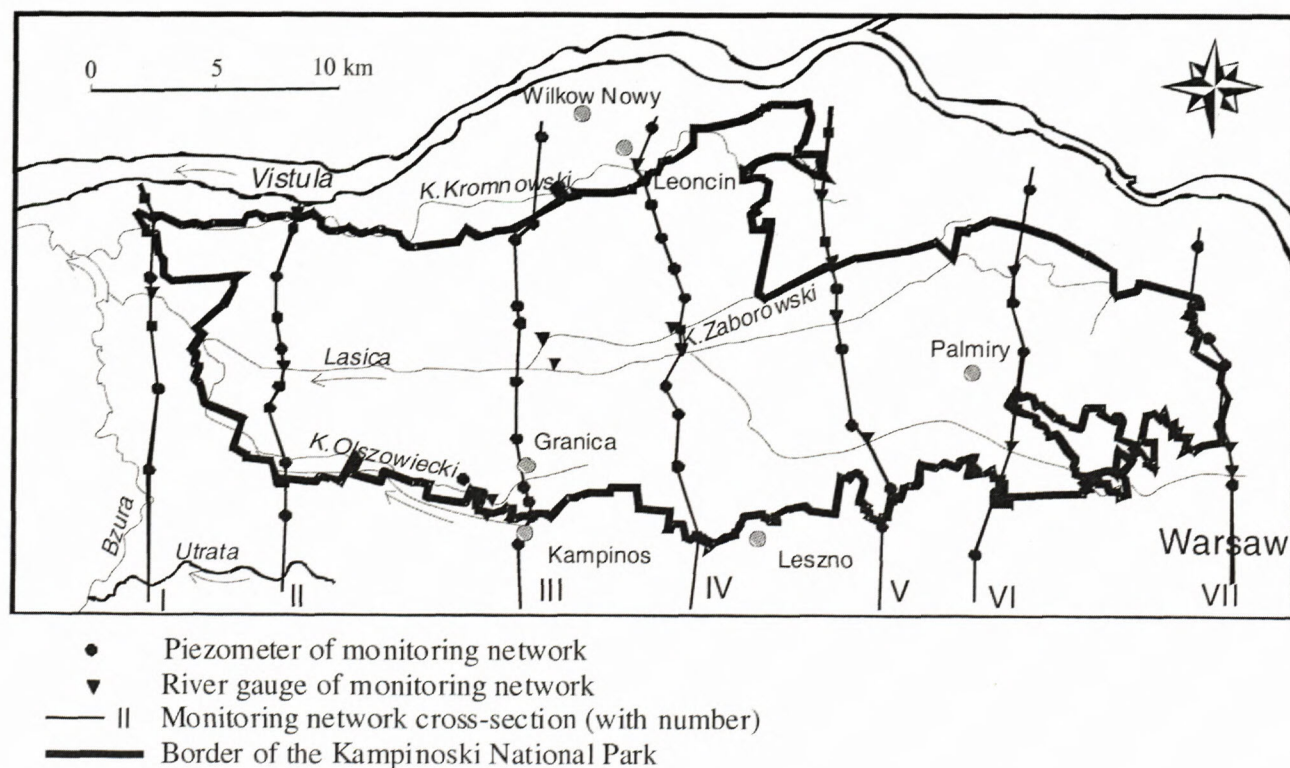


Fig. 2. Monitoring network in the Kampinoski National Park.

Tab. 1. Hydrogeological characteristic of hydrodynamic zones in the KNP.

Hydrodynamic zone	Average depth /ordinate of groundwater table [m b.t.l.] / [m a.s.l.]	Level fluctuation range [m]	Hydraulic conductivity [$\times 10^{-5}$ m/s]
Northern dune zone	1.30 – 4.49 / 68.04 – 73.44	0.6 – 1.76	12.21
Southern dune zone	1.27 – 4.38 / 68.60 – 77.88	0.85 – 1.18	5.57
Northern swampy zone	0.86 – 1.74 / 68.19 – 73.93	0.85 – 1.67	7.39
Southern swampy zone	0.61 – 2.48 / 69.05 – 81.81	0.64 – 1.5	5.32
Vistula flood plains	0.89 – 4.33 / 65.67 – 75.70	0.58 – 1.93	19.38
Bzura terrace	2.57 – 4.70 / 66.63 – 68.19	0.98 – 1.23	12.75
Warsaw suburbs	1.33 – 3.30 / 78.01 – 97.53	0.81 – 1.92	6.38
Blonie Level	1.87 – 3.27 / 82.97 – 91.83	1.2 – 2.09	3.85

sands, in some places silty. The groundwater table has an unconfined character.

In the vertical profile, three fundamental sediment series with various filtration parameters determined by in-situ investigations:

- horizon of medium grained sands, in some roof places passing into silty sands, with numerous interbeddings of washed out boulder clays, gravel with very diversified permeability parameters ($k = 0.9 \div 19$ m/d, $k_{av} = 6.3$ m/d) with a thickness of 10 to 15 m,
- middle horizon, gravel-sandy ($k = 1.3 \div 19.8$ m/d, $k_{av} = 8.5$ m/d) with a thickness of 8 to 15-20 m,
- subsurface sand horizon ($k = 0.4 \div 20$ m/d, $k_{av} = 18$ m/d) with a thickness of 3 to 6 m.

Aquifer hydraulic conductivity values were also determined by statistical analysis of hydrological data, obtained from approximately 980 wells, located within the study area (Krogulec, 2003). Average hydraulic conductivity value for the aquifer sediment was determined from pumping test results to be 47.7 m/d (range of 1.2 m/d to 89.6 m/d).

2.3 Conditions of groundwater recharge and drainage

Groundwater recharge takes place almost exclusively as a result of infiltrating precipitation but a second recharge source comes from a lower aquifer. The lower aquifer from Blonski Level only affects the southern part of Kampinos Terrace. During high spring runoff, water from the Vistula river may infiltrate the aquifer. Water also infiltrates from the Bzura river in the south-western part of study area.

The infiltration value depends mainly on the lithology of the subsurface and terrain afforestation ratio. The values of infiltration were obtained by mathematical modelling, hydrograph separation and table fluctuation (WTF) method.

Modelling calculations were performed using VisualMODFLOW 2.20 software; simulations have been made with the use of the Strongly Implicit Procedure Package – SIP (McDonald and Harbaugh 1988) digital method. The values of infiltration obtained by modelling calculation are:

- in the southern swampy zone – 332 mm/year
- in the northern swampy zone – 186 mm/year
- in the Vistula river flood plain – 55.5 mm/year

The runoff separation to surface and underground component by hydrograph separation was made using automated method so called, **Base Flow Index** (Magnuszewski, 1990; Tomaszewski, 1998). The quantitative evaluation of Lasica base runoff (catchment located in KNP area – 441.0 km²) depends on the intensity. Volume of precipitation entitles us to state that it plays an important role in the lowland drainage basin with swamps and forest cover. Series of daily discharge in have been used. In the period 1951-2000 the river base runoff varies considerably: from 163 mm in 1967 to barely 43 mm in years 1952 and 1992 (Soczyńska et. al., 2003).

Water table fluctuation (WTF) method is a conventional method for quantifying groundwater infiltration recharge by multiplying the specific yield to the water level rise (Healy and Cook, 2002). Based on the van Genuchten model, an analytical relationship between groundwater recharge and the water level rise is derived. The equation is used to analyse the effects of the depth to water level and the soil properties on the recharge estimate using the WTF method. The values of infiltration obtained by WTF method (observation from KNP monitoring network) are from 73 mm/year in flood terrace of Vistula and in swamp areas to 265 mm/year in dunes areas.

Empirical method offers a quick assessment of infiltration recharge in terms of climate, land use, terrain and geology. Results of infiltration using empirical method in KNP area are from 119 in swamp areas to 199 mm/year in dunes.

Analysis of the balance elements on numerical model shows that from the south of the Kampinos Terrace is recharge by water from the deeper aquifer of the Blonie Level. The supply value in the study area is 0.2 m³/d for 1 m of slope width (Krogulec, 1997).

Aquifer drainage on the Kampinos Terrace takes place by rivers and canals and partially with evapotranspiration processes in the swampy areas. The Vistula river has the strongest drainage character and is the regional drainage base. Similarly an important role in

drainage of aquifer fulfils Bzura, mostly in its lower section. Drainage of the aquifer also takes place through production of groundwater in many points in the study area.

The numerical model research confirmed the prevailing role of the Vistula river in forming of the hydrodynamic regime in the analysed valley unit. The river is a regional drainage base, supplied by groundwater volume of 0.55 m³/d for 1 m of river length. The remaining water flows drain the aquifer with the following volumes: Olszowieckie A and B canals – 0.29 m³/d, Lasica river – 0.34 m³/d, Kronowski canal – 0.12 m³/d. The groundwater drainage in the study area is also related to the evapotranspiration process which is significant only in the depressions and on the flood plain where the groundwater table not exceeds 1.5 m below terrain level. In the northern swampy zone the evapotranspiration value is 0.31 m³/d, in the southern swampy zone – 0.16 m³/d, in the Vistula river flood plain – 0.084 m³/d (Krogulec, 2004).

Annual average sum of potential evaporation in the Lasica catchment in the period of 1951-2000 calculated by the Penman method is 722 mm. Prevailing part (76 %) occurs in the warm half-year (546 mm), while 176 mm (24 %) represents cold half. Average monthly sums are from 15 mm in January and December to nearly 10 times bigger (121 mm) in July (Soczyńska et al., 2003).

3. Groundwater vulnerability

In this article groundwater vulnerability to contamination is understood to be a natural characteristic of the aquifer system. It describes the risk of migration of hazardous substances from the surface to the aquifer. Intrinsic vulnerability is determined only by hydrogeological conditions (recharge conditions, discharge, formation conditions including degree of groundwater isolation). Specific vulnerability also takes into consideration type of hazardous substance, its amount, and its location with respect to the aquifer (Duijvenbooden and Waegening, 1987; Vrba and Zaporozec 1994; Witczak and Żurek, 1994).

For central area of KNP located in Vistula river valley, natural vulnerability of groundwater was determined with application of two methods:

- U.S. EPA DRASTIC Model (Aller et al., 1987),
- travel time of conservative contamination from the terrain surface (percolation time through aeration zone).

3.1 DRASTIC model

One of the most widely used groundwater vulnerability methods is DRASTIC, developed by the United States Environmental Protection Agency (EPA) as a method for assessing groundwater pollution potential (Aller et al., 1987). As was mentioned above, it is one of the most popular ranking methods developed especially for evaluation of vulnerability in the particular hydrogeological regions. Classification system (evaluation) of vulnerability in the DRASTIC method is the standard tool used by many countries in management of water resources, water legislation and controlling. In

Poland DRASTIC was used to evaluate vulnerability of geological variability (porosity reservoir, porosity-fracture, fracture) of Ścianawka catchment, with the area of 595 km², located in Lower Silesia (Limisiewicz, 1998) and Silesia catchment (Witkowski et al., 2003), and also was used in some studies for various types of water bearing reservoirs, mostly of porosity-fracture type, done by Academy of Mining & Metallurgy (Witczak and Żurek, 1994).

In the DASTIC method is an acronym for the variables that control the groundwater pollution potential (depth to the water level, effective infiltration, aquifer media, type of soil, topography, impact of vadose zone, has the permeability coefficient of aquifer). Each variable are assigned different degree of importance on a scale of 1 to 5. Each criterion also possesses suitable order of value of the used coefficient and is credited with a rank, in other words a rank on 1 to 10 scale (Tab. 2). Vulnerability index IPZ_Σ that is the sum of the multiplication of variable rank and weight of individual criteria is the final evaluation of groundwater vulnerability.

$$IPZ_{\Sigma} = \sum_{n=1}^7 (\text{variable rank} \times \text{weight of criterion})$$

The DRASTIC method assumes that the flow of the groundwater is linear. This assumption is fully acceptable for the porous media in the aquifer of the central Vistula river valley. Final evaluation of vulnerability depends on the precision and accuracy of hydrological character, which is very high for KNP region. Assignments of each criterion (hydrogeological data, soil assignments, and topography) were plotted on several maps (scale 1 : 50 000) with the use of vectoring, calculations and visualizations in the following computer programs: ARC/INFO 8.0.1, ArcView 3.2, AVSpatialAnalyst 1.1, AVArcPress 2.0 produced by ESRI, operating on Sun Solaris and Win NT platforms. Modeling called for all criteria to be brought into a form of pseudo-continuous distributions, expressed in a form of nets of natural mesh with a resolution of 100 m x 100 m (block 100 x 100 m, more than 65 000 blocks).

Basing on the initial data and calculations conformable with DRASTIC methods slightly modified but conforming to the specifics of the study area, classification of groundwater vulnerability was obtained, dependent on the range of the IPZ index. The following types of groundwater vulnerability were assigned: very low (IPZ_Σ < 100), low (IPZ_Σ from 100 to 125), medium (IPZ_Σ from 126 to 150), moderately high (IPZ_Σ from 151 to 175), high (IPZ_Σ from 176 to 200), very high (IPZ_Σ > 200).

The middle Vistula river valley is characterized by moderate (37 % of the area or 228 km²) and moderately high (52 % of the area or over 318 km²) vulnerability to contamination. In the study area about 12.5 km² is an area of high vulnerability. Remaining vulnerability classes are located on considerably smaller areas (Tab. 3).

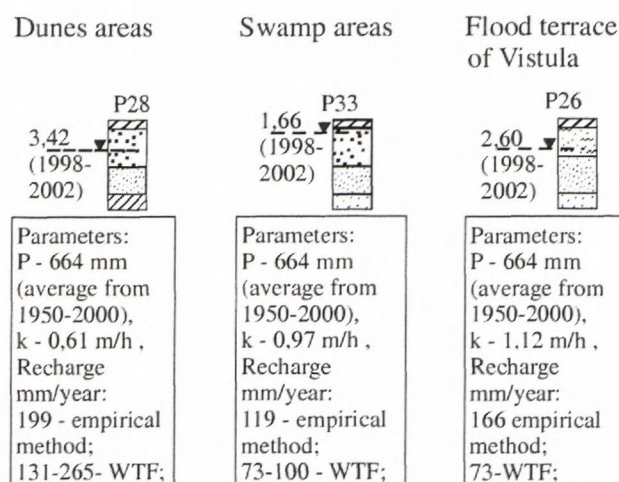
The DRASTIC evaluation produces a map that shows the distribution of values of the vulnerability index IPZ_Σ (scheme of map - Fig. 2).

Tab. 2. Rating and weight of criterion for DRASTIC criteria with assigned weights (after Aller, et al., 1987 – modified for KNP area - Krogulec, 2004).

No	Criterion	Classes of criterion	Weight of criterion	Rank
1 D	Depth to groundwater water table [m]	>5 m 3.1-5 m 1.1-3 m <1 m	5	7 8 9 10
2 R	Net Recharge [mm/year]	50-75 101-130 151-180 181-250 >250	4	2 3 4 5 6
3 A	Lithology of Aquifer	sandy clay, loam, loam and sands sandy loam, sands sands, sandy loam sands sands, gravel	3	2 3 4 6 8
4 S	Soil media	loam sandy loam shrinking clay peat thin anthropogenic absent	2	5 6 7 8 9 10
5 T	Topography (slope) [%]	2.9-3.9 2.5-2.9 2.0-2.5 1.6-2.0 1.0-1.6 1.0-0.0	1	75 8 8.5 9 9.5 10
6 I	Impact of aeration zone	clay silty loam loam sands sands, gravel	5	2 3 4 6 8
7 C	Permeability Coefficient of aquifer [m/day]	<4 4-12 13-28 29-40 41-80	3	1 2 4 6 8

Tab. 3. Distribution of the vulnerability classes – DRASTIC model.

IPZ _Σ	Classes of the relative vulnerability	Area [km ²]	Percentage share of classes
<100	very low	0.01	0.002
100-125	low	52.82	8.63
126-150	medium	228.05	37.25
151-175	medium high	318.86	52.08
176-200	high	12.53	2.05
>200	very high	0.03	0.005
Σ	612.3 km ² – area of hydrogeological unit		100 %



P33 - number of piezometer in KNP monitoring network;
P - precipitation; k - coefficient of permeability

Fig. 3. Characteristic of hydrodynamic zones within the Kampinoski National Park.

$$t_a = \sum_{i=1}^n \frac{m_i \cdot (w_0)_i}{I_e}$$

where:

m_i - thickness of successive layers of aeration zone profile [m]

w_0 - average volumetric moisture of successive layers of aeration zone [-]

I_e - infiltration of atmospheric precipitation deep into the soil profile [m/year]

Travel time of conservative contamination through aerated zone ($t = t_a + t_p$) is a sum of infiltration through aerated zone (t_a) and eventual percolation through deeper cover (t_p). This is the reason why separate calculations were performed for the soil layer cover (average thickness in the studied area = 35 cm) and for the remaining aerated zone thickness. The result is the sum of flow time through both zones.

Infiltration time, determined by mentioned formula is from 0.5 to 10 years, but almost 75 % of the study area is

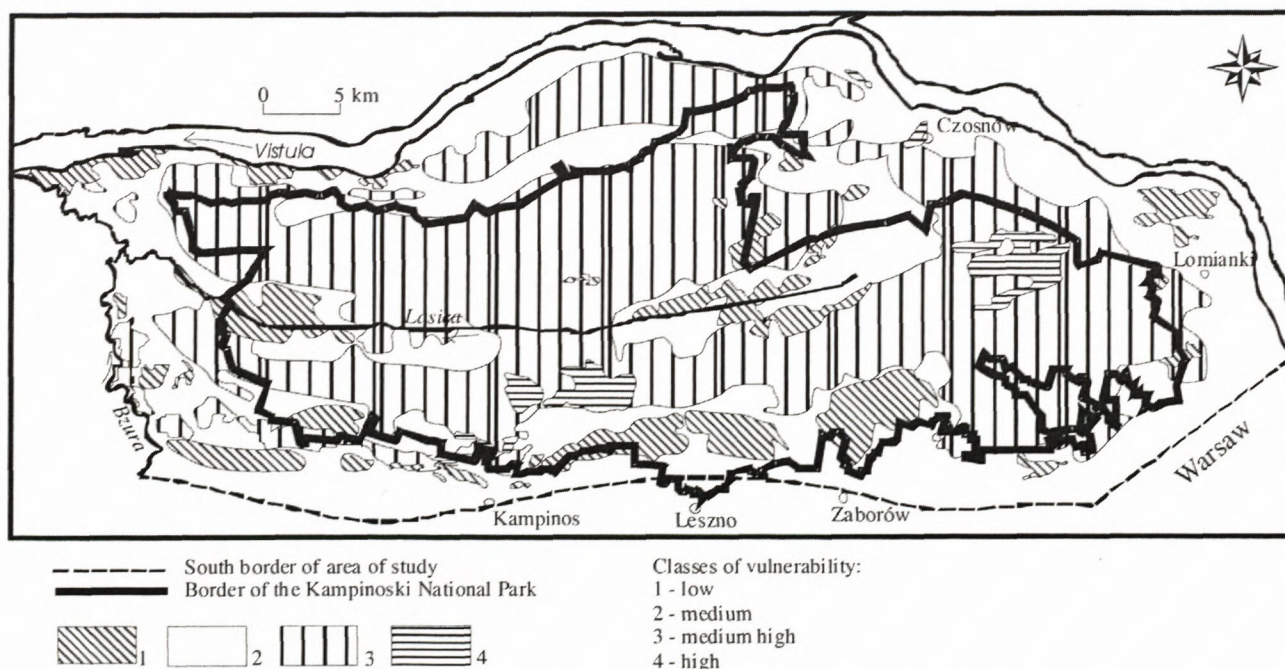


Fig. 4 Groundwater vulnerability map of the Kampinoski National Park based on DRASTIC method.

3.2 Travel time of conservative contamination from the terrain surface (percolation time through aeration zone) as a criterion of vulnerability

Estimation of travel time of conservative contamination from the terrain surface - infiltration time is a key factor in determining the vulnerability of groundwater. It is one of rational criteria used in evaluating groundwater vulnerability. Approximate determination for travel time can be achieved by the time of water exchange in a rock formation assuming piston - flow model.

Infiltration time through the aerated zone was calculated with the use of following formula (Wosten *et al.*, 1986; Haith and Laden, 1989; Witczak and Żurek, 1994):

characterized by an infiltration time from 0.5 to 3 years (high class of vulnerability).

Because evaluation methods of groundwater vulnerability to contamination are not standardized, it is difficult to compare results and conclusions between studies potential impacts (Tab. 4).

4. Conclusion

Detailed hydrological recognition and also data relating to topography and soil layering of KNP region become the basis for compiling reliable and precise database. Use of GIS techniques during creation of vulnerability map, made it possible for much more precise assignment of data (value) to each criterion, more precise division of

Tab. 3. Travel time of conservative contamination in Vistula River valley (area of the Kampinoski National Park), percentage share of classes.

Vulnerability classes	Migration time of conservative contamination [year]	Percentage share of classes
Very low	>30	0.6
Low	25-30	0.2
	20-25	1.0
Medium	15-20	0.3
	10-15	7.9
Medium high	5-10	2.6
	3-5	8.1
High	1-3	64.7
	0.5-1	10.0
Very high	0.083-0.5	4.2
	<0.083 (30 days) ¹⁾	0.4

¹⁾ – according to Polish Low (till 2001 year) – range of intake protection zone

Tab. 4. Distribution of percentage share of vulnerability classes: DRASTIC and travel time methods.

Classes of the groundwater vulnerability	Percentage share of classes – DRASTIC method	Percentage share of classes – travel time method
Very low	0.002	0.6
Low	8.63	1.2
Medium	37.25	8.2
Medium high	52.08	10.7
High	2.05	74.7
Very high	0.005	4.6

vulnerability types depending on IPZ value. Method used, even though it might bring on some mistakes, seems to be correct in case of hydrological unit of valley type. Special attribute of the surveyed area are a long-term hydrological recognition, which in effect yields data regarding positioning of groundwater layer in all assigned zones within KNP area.

DRASTIC method enabled creation of general classification as well as map of natural vulnerability for the study area, based on calculated values of the IPZ index. This may be useful tool for environmental management. For areas where groundwater table in porous medium is shallow – river valley, and not isolated by low permeability natural from the terrain surface, for example in river valleys, an additional method to use is the migration time of conservative contamination from the terrain surface. Supplementing the base DRASTIC model can be conducted for an entire study area of study or selected parts, characterized by high natural vulnerability or perhaps in cases where there are planned changes in development. The resulting maps of groundwater vulnerability, obtained from U.S. EPA DRASTIC, show that in river valley - area of study is generally characterized by medium and medium high vulnerability (nearly 90 % of study area). The travel time of conservative contamination from

terrain surface is an important factor for quantifying the groundwater vulnerability. Travel time in KNP area is from <30 days to 30 years but almost 75 % of the study area is characterized with the time from 0.5 to 3 years. It shows the high class of vulnerability.

Calculations performed with different methods; in this case using different parameters (in consequence different maps) can become basis for scenario maps showing varying concepts for protection of groundwater depending on terrain development.

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Exotic pyrope–almandine garnets in the Lukáčovce Mb. (Quaternary)

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Abstract: The Lukáčovce Mb. presents sediments of the alluvial fan formed by braided river(s) in areas of the Nitrianska pahorkatina Upland and of the Trnavská pahorkatina Upland. Detritic garnets were separated in fraction from 0.25 down to 0.10 mm and analysed by microprobe. Acquired results were compared with other analyses of garnets from various Slovak rock types. In the Lukáčovce Mb. occur four types of garnets: 1) Almandine and almandine-spessartite garnets derived mainly from paragneisses, in tributary sources maybe from pegmatites; 2) Almandine-spessartite-grossular garnets came from rocks with low-grade metamorphism (mica schists; eventually phyllites); 3) Almandine-grossular-pyrope garnets which are following trend of mica schists, volcanites, amphibolites and amphibolized eclogites. 4) The last type are pyrope-almandine garnets with content of pyrope molecules from 27 % to 45 %. Composition of the first three garnet types suggests the source area formed by the crystalline complex of the Považský Inovec Mts. and neovolcanites. This source responses to results of petrographic analyses of gravels and also to analyses of heavy minerals. The primary source of pyrope-almandine garnets was not described in Slovakia until now. Similar garnets were analysed so far only as detrital grains in Jurassic carbonates of the Klippen Belt and of Central Carpathians (Aubrecht and Méres; 2000).

Key words: garnet, Lukáčovce Mb., alluvial fan

Introduction

Analysed garnets are component of heavy fraction in the Lukáčovce Mb. The Lukáčovce Mb. was formed in the area of the Nitrianska pahorkatina Upland and of the Trnavská pahorkatina Upland from of Upper Pliocene till Mindel (Fig. 1), during hot and dry climate with some periods of intensive rainfalls (Šarinová, 2004). They were deposited in form of alluvial fan caused by braided river(s). Within their grain size composition it is possible to detach weaker sorted, lesser mineral matured sands (sulitharenites) with content of gravel above 17 %; and better sorted, mineral more matured sands (subarkose) with content of gravel up to 5 % (sorting = 0.65 to 3.7 ϕ ; $M_z = -0.6$ to 3.7 ϕ). Gravels fillings of river channels are sporadic. Within heavy fraction there are present limonite, ilmenite, hematite, magnetite, tourmaline, garnet, staurolite, zircon, rutile, epidote and in accessory amounts also sillimanite, kyanite, monazite and cromite. In fillings of riverbeds is present gold too. Clay fraction includes clastic quartz, kaolinite, illite and smectite \pm goethite. Clasts of gravel size are composed by lower Triassic sandstones, glauconitic sandstones, quartz, organogenic and volcanogenic silicites and in smaller amount by granitoids and freshwater sandy limestones. There are present Fe–Mn concretions with peas size and secondary Ca–concretions too. Petrographic composition of gravels and heavy fraction is suggested having source in crystalline complex of the Považský Inovec Mts. Secondary sources consist of Neogene filling of basins. A part of material is derived from neovolcanites (rutiles with inclusions of trachydacite, basanite to the basalts composition melt, silicified volcanic glass with

magmatic corroded quartz or with post lamellar crystals pseudomorphs), namely straight from neovolcanites alternatively they are redeposits from Neogene fillings of the basins.

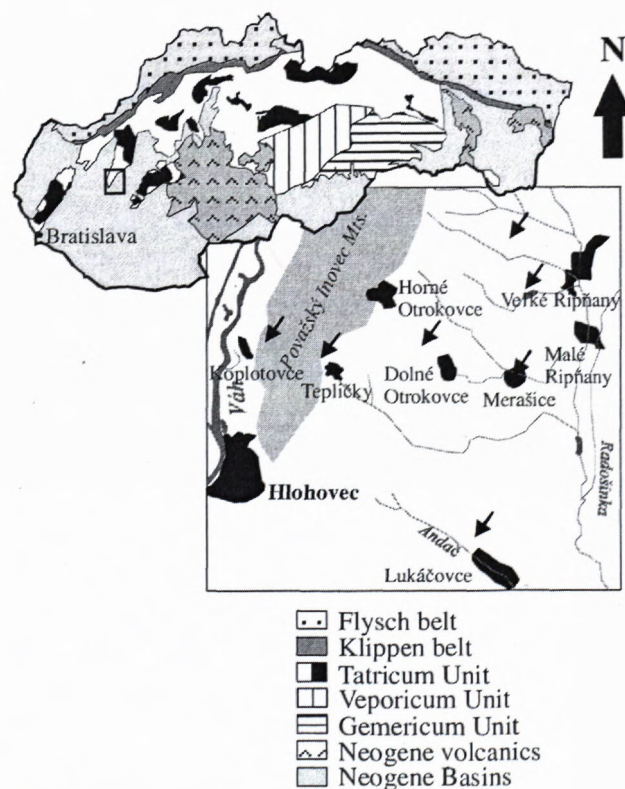


Fig. 1. Map of studied area (arrows – localities of the Lukáčovce Mb.).

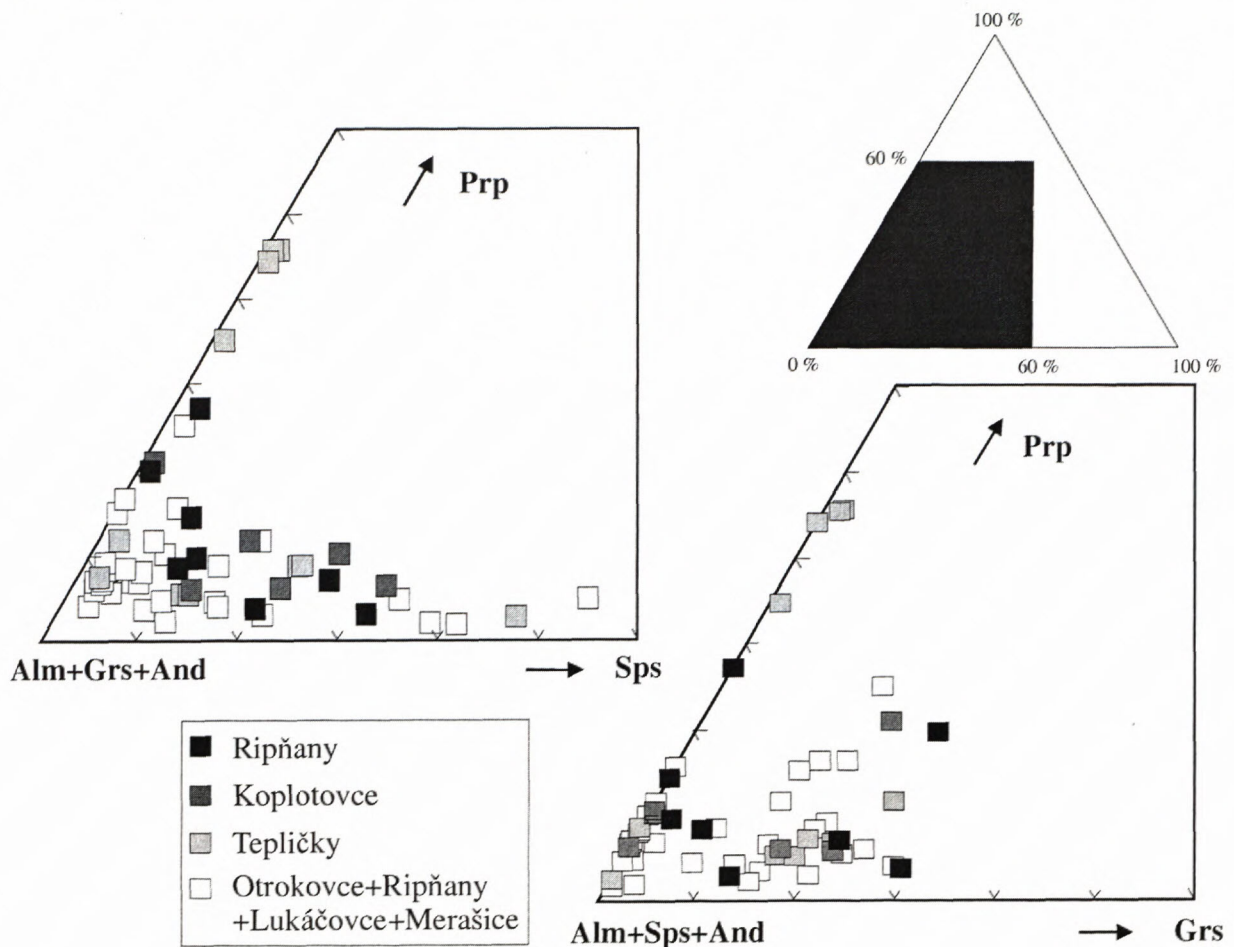


Fig. 2. Distribution of garnets in studied localities (Alm – almandine, Sps – spessartite, Grs – grossular, Prp – pyrope, And – andradite).

This work aims to determine the source rocks by crystallochemical composition of garnets, and mainly to determine the source of exotic pyrope–almandine garnets with content of pyrope molecule over 30 %.

Share of garnet in the heavy fraction is moved from 2 up to 4 %; mainly in coarse-grained samples the garnet fraction is increased (from 8 up to 13 %). Grains are often angular, without optical zonation. Pink coloured garnets were dominant.

Method

There were analysed 43 detritic garnets corresponding to fraction 0.25–0.10 mm. Chemical composition of garnets was determined by the instruments CAMECA SX 100 and HITACHI S – 4700. A portion of garnets was point-wise analysed (core – rim). Separate analysis was performed on garnets from localities Tepličky, Ripňany nad priehradou and Koplotovce. Garnets from localities Lukáčovce, Merašice, Otrokovce and Ripňany nová piesočnica were analysed together (Fig. 2). Total number of analyses was 57. Obtained analyses were re-counted to the base of 8 cations. For identification of the source rocks of garnets there were used 420 published and unpublished analyses of garnets from various Slovak rocks, elaborated by different authors, which were calculated in the identical way.

Results

All garnets were splitted into four types on the basis of predominating molecules (Tab. 1; Fig. 3a; Prp – pyrope, Alm – almandine, Sps – spessartite, Grs – grossular, And – andradite). Point-wise analyses (core – rim) within the scope of a grain suggested to very small chemical changes in the garnet grain center – rim composition (Fig. 3b, Tab. 2).

First garnet type: Formed by almandine and almandine-spessartite garnets (Alm 68–85 %; Sps 2–52 %), with content of pyrope molecules 2–14 %. Content of grossular molecule varies from 0 to 2 %. This garnets type had the biggest share (38.8 % of analyses); and it was found in all localities.

Second garnet type: Created by grossular – spessartite – almandine garnets (Alm 51–73 %, Sps 8–31 %, Grs 7–32 %), with content of pyrope and andradite molecules from 3 up to 7 %. This garnets type had represented 24.56 % of all analyses, and it was found in all localities.

Third garnet type: Consisting of garnets of pyrope – grossular – almandine composition (Alm 52–65 %, Grs 14–27 %, Prp 5–25 %), with content of spessartite and andradite molecules up to 5 %. These garnets formed 28.07 % of all analyses. It is possible to divide third garnet type into two separate groups. *First group* of garnets has affinity toward the garnets of second type. Into

Tab. 1. Selected representative analyses garnets of the Lukáčovce Mb. (calculated by 8 cations; CAMECA SX-100.)

garnet sample	type 1		type 2		type 3		type 4	
	LV-2	LV-5	R-8	K-4	K-5	T-3a	T-4a	T-6
SiO ₂	36.93	36.21	37.55	37.31	38.86	36.00	39.23	37.64
TiO ₂	0.06	0.06	0.16	0.08	0.11	0.09	0.03	0.00
Al ₂ O ₃	20.86	20.48	20.97	20.98	21.74	19.82	21.99	21.42
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.02	0.02	0.04	0.04
FeO	38.51	19.45	20.75	25.43	27.26	30.87	24.07	28.31
MnO	1.94	22.84	11.39	9.49	0.46	1.00	0.47	0.49
MgO	2.05	1.16	1.80	1.51	5.48	1.78	12.05	8.93
CaO	0.48	0.19	8.26	6.43	7.61	8.73	1.54	1.35
Na ₂ O	-	-	-	-	-	0.00	0.02	0.03
Total	100.83	100.39	100.88	101.230	101.54	98.30	99.43	98.22
Si	2.985	2.958	2.977	2.969	2.987	2.935	2.979	2.958
Al T	0.015	0.042	0.023	0.031	0.013	0.065	0.021	0.042
ΣT	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
AL Y	1.972	1.929	1.936	1.936	1.956	1.840	1.947	1.942
Ti	0.004	0.004	0.010	0.005	0.006	0.005	0.002	0.000
Cr	0.000	0.000	0.000	0.000	0.001	0.001	0.002	0.003
Fe Y	0.024	0.067	0.055	0.059	0.037	0.153	0.049	0.056
ΣY	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Fe X	2.579	1.262	1.321	1.633	1.716	1.952	1.479	1.805
Mg	0.247	0.141	0.213	0.179	0.628	0.217	1.364	1.046
Mn	0.133	1.580	0.765	0.640	0.030	0.069	0.030	0.033
Ca+Na	0.042	0.017	0.702	0.548	0.627	0.763	0.127	0.116
ΣX	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
prp	8.234	4.709	7.091	5.970	20.929	7.229	45.465	34.873
sps	4.427	52.675	25.492	21.319	0.998	2.298	1.012	1.092
alm	85.954	42.062	44.032	54.438	57.184	65.051	49.305	60.155
grs	0.163	0.000	20.652	15.319	18.997	17.679	1.657	0.965
and	1.222	0.554	2.734	2.954	1.831	7.669	2.453	2.788
uvr	0.000	0.000	0.000	0.000	0.061	0.074	0.108	0.127

this group belong garnets with lower content of pyrope molecules (below 10 %). *Second group* formed garnets with pyrope over 10 %.

Fourth garnet type: The last, fourth garnet type is created by mentioned exotic pyrope–almandine garnets (Alm 49–66 %, Prp 27–45 %; other molecules up to 2 %). This type of garnets covered only 8.77 % from analyses; and so far such garnets were analysed only from localities Tepličky and Ripňany nad priehradou.

Discussion

Composition of garnets of *first type* (almandine and almandine-spessartite garnets) corresponds mainly to analyses of paragneisses garnets (Fig. 4), especially to the garnets from paragneisses originated at temperatures from 450 up to 600 °C (biotitic, biotite-sillimanite and staurolite paragneisses from the Považský Inovec Mts., Tríbeč Mts., Suchý Mts., Malá Magura Mts., Malé Karpaty Mts., Spišsko-gemerské rudohorie Mts.; Dyda, 1981, 1990, 2002; Hovorka et al., 1987; Méres and Hovorka, 1989; Faryad, 1996; Zafko and Broska, 1996;

Vozárová – unpublished). These garnets do not overlap with analyses from higher temperature paragneisses (650–700 °C; Branisko Mts., Malá Fatra Mts.; Hovorka et al., 1987; Méres and Hovorka, 1989; Faryad, 1995; Vozárová and Faryad, 1997). They are corresponding fairly with the composition of garnets from paragneisses of the Považský Inovec Mts. and Tríbeč Mts. (Fig. 5; Zafko and Broska, 1956; Vozárová – unpublished). One part of garnets is overlapping with analyses of garnets from pegmatites, too (Fig. 6; Malé Karpaty Mts. – Dávidová, 1968) and neovolcanites – andesites (Fig. 6; Zorkovský, 1956 in Kaličiak et al., 1988; Harangi et al., 2001).

Composition of garnets of *second type* (grossular – spessartite – almandine garnets) is similar mainly as garnets from mica schist and phyllites (Veporicum – Vozárová, unpublished), what suggests their origin in the metamorphic rocks of lower grade – mica schist of the Považský Inovec Mts. (Fig. 7). Amphibolites also reach the field of second garnet type occurrence, but only marginally (Fig. 8), particularly garnets from leptynite–amphibolite complex of the Tríbeč Mts. (Fig. 5; Hovorka and Méres, 1990).

Third garnet type (pyrope – grossular – almandine): *First group* with lower content of pyrope molecules (below 10 %), has originated from lower metamorphosed rocks (mica schist and phyllites – Fig. 7) following comparison. *Second group*, garnets (with pyrope over 10 %) resemble mainly garnets from amphibolites, amphibolized eclogites and neovolcanites (Figs. 6 and 8). Garnets with content of pyrope molecules from 10 up to 15 % respond to garnets from neovolcanites – andesites in composition (Fig. 6; Veľký Šariš – Zorkovský, 1956 in Kaličiak et al., 1988; Visegrád Mts., Börzsöny, Central Slovakian Volcanic Field – Harangi et al., 2002) and also to garnets from amphibolites of Branisko Mts., Spišsko-Gemerské rudohorie Mts., Malá Fatra Mts., which were metamorphosed at lower temperatures (490–650 °C at 5 kBar – Spišiak and Hovorka, 1985; Hovorka et al., 1992; Faryad, 1995; Vozárová, Faryad, 1997; Fig. 8). Garnets with content of pyrope molecules from 17 up to 22 % correspond to garnets from metabasites of Branisko Mts. (Faryad, 1996; Méres et al., 2000), which were metamorphosed in eclogite facies (600–770 °C, 8–10 kBar) with subsequently retrograde metamorphism under conditions of amphibolites facies (Fig. 8). Therefore, we can consider mica schists of Považský Inovec Mts., neovolcanites and eventually amphibolites of the Považský Inovec Mts. and Tríbeč Mts. to be the source of the third type garnets. None analyses of garnets with content of pyrope molecules above 17 %, which would correspond to amphibolized eclogites, I was able to obtain/found from the Považský Inovec Mts. or Tríbeč Mts.

Exotic pyrope–almandine garnets of *fourth type* from the Lukáčovce Mb. are by their lower bound touched to paragneisses composition from Branisko Mts. and Malá Fatra Mts., what were originated from rocks metamorphosed at temperatures from 700 up to 730 °C and under pressure of 7–8 kBar (Faryad, 1996). However, content of pyrope molecules from 30 to 45 % (locality Tepličky)

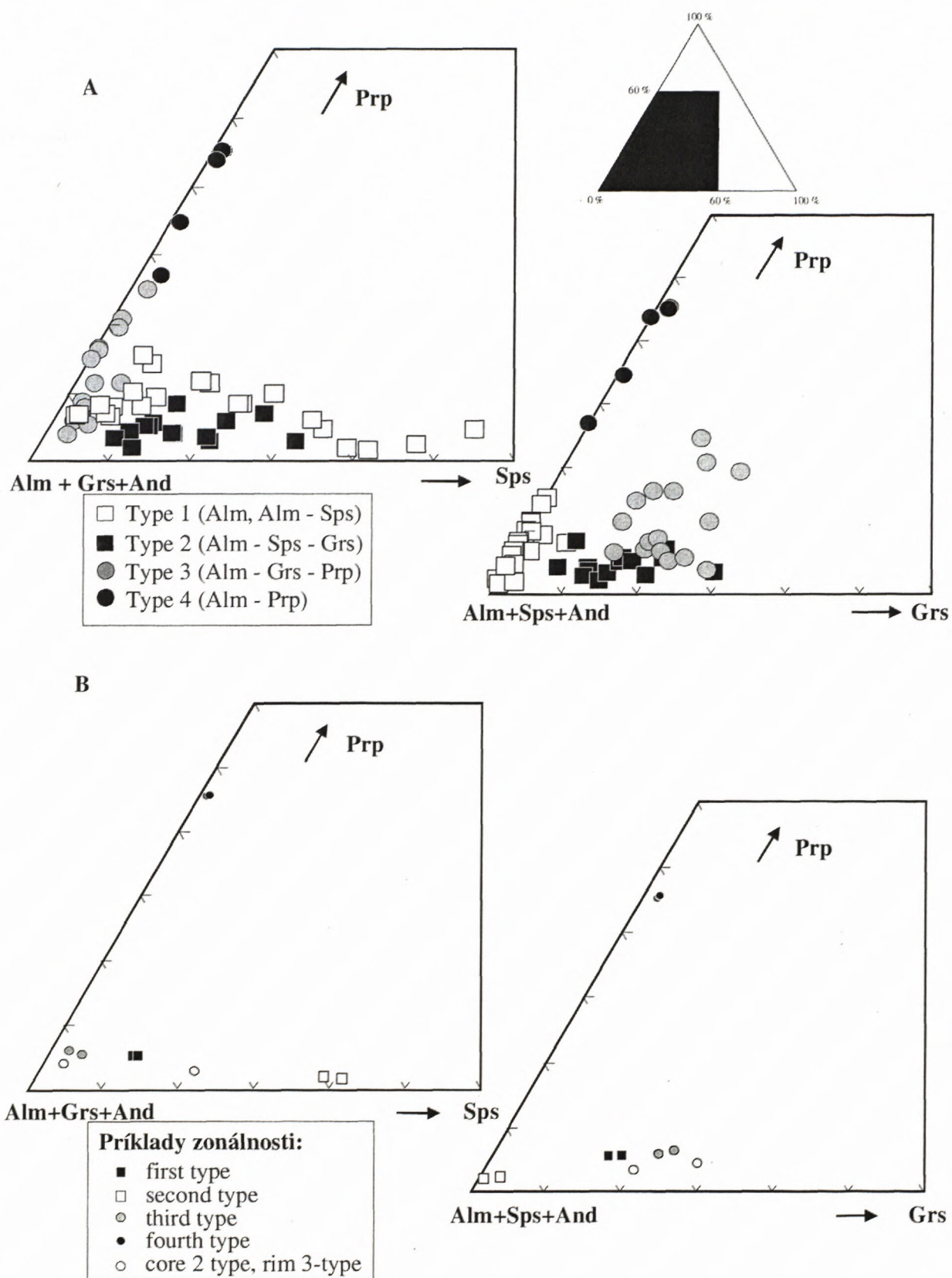


Fig. 3A. Distribution of garnets of the Lukáčovce Mb. on base of their chemical composition. B – Samples of chemical zonality which occurred in particular types of garnets (Alm – almandine, Sps – spessartite, Grs – grossular, Prp – pyrope, And – andradite).

Tab. 2. Samples of chemical zoning of the garnets of the Lukáčovce Mb. (Fig. 3 b; A - center, B - rim; calculated by 8 cations; CAMECA SX-100, *HITASCHI S-4700.)

Garnet	Type 1		Type 2		Type 3		Type 4		Max. zonal garnet	
Sample	pl 4a*	pl 4b*	T-1a	T-1b	pl 10a*	pl 10b*	T-4a	T-4b	pl 5a*	pl 5b*
SiO ₂	35.30	34.50	36.46	37.21	35.96	36.05	39.23	39.39	35.90	36.96
TiO ₂	0.15	0.23	0.12	0.11	0.13	0.00	0.03	0.00	0.08	0.08
Al ₂ O ₃	18.09	18.51	19.91	20.13	19.45	19.86	21.99	21.90	19.62	19.62
Cr ₂ O ₃	0.00	0.14	0.02	0.03	0.10	0.00	0.04	0.07	0.00	0.00
FeO	22.80	22.36	28.74	28.70	28.62	28.86	24.07	23.91	23.66	27.47
MnO	16.04	17.18	5.30	5.08	1.94	1.07	0.47	0.55	8.88	1.21
MgO	0.49	0.44	1.31	1.34	1.33	1.45	12.05	12.07	0.74	0.95
CaO	4.58	4.14	7.35	7.42	9.29	9.48	1.54	1.51	8.49	10.91
Na ₂ O	-	-	0.02	0.02	-	-	0.02	0.02	-	-
Total	97.45	97.50	99.24	100.03	96.82	96.77	99.43	99.41	97.37	97.20
Si	2.972	2.907	2.964	2.997	2.979	2.979	2.979	2.991	2.973	3.040
Al T	0.028	0.093	0.036	0.003	0.021	0.021	0.021	0.009	0.027	0.000
ΣT	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.040
Al Y	1.767	1.745	1.872	1.908	1.878	1.913	1.947	1.951	1.888	1.902
Ti	0.010	0.015	0.007	0.006	0.008	0.000	0.002	0.000	0.005	0.005
Cr	0.000	0.009	0.001	0.002	0.007	0.000	0.002	0.004	0.000	0.000
Fe Y	0.224	0.231	0.120	0.083	0.108	0.087	0.049	0.045	0.107	0.093
ΣY	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Fe X	1.382	1.345	1.834	1.851	1.875	1.907	1.479	1.474	1.532	1.797
Mg	0.061	0.055	0.158	0.161	0.164	0.179	1.364	1.366	0.091	0.117
Mn	1.144	1.226	0.365	0.347	0.136	0.075	0.030	0.035	0.623	0.084
Ca+Na	0.413	0.374	0.642	0.642	0.825	0.839	0.127	0.125	0.753	0.962
ΣX	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	2.960
prp	2.050	1.842	5.280	5.353	5.475	5.954	45.465	45.549	3.046	3.937
sps	38.126	40.871	12.164	11.564	4.537	2.496	1.012	1.171	20.765	2.849
alm	46.053	44.827	61.148	61.688	62.503	63.573	49.305	49.127	51.076	60.722
grs	2.585	0.449	15.348	17.134	21.776	23.619	1.657	1.718	19.787	27.789
and	11.186	11.543	5.986	4.158	5.382	4.357	2.453	2.228	5.327	4.704
uvr	0.000	0.466	0.074	0.102	0.327	0.000	0.108	0.207	0.000	0.000

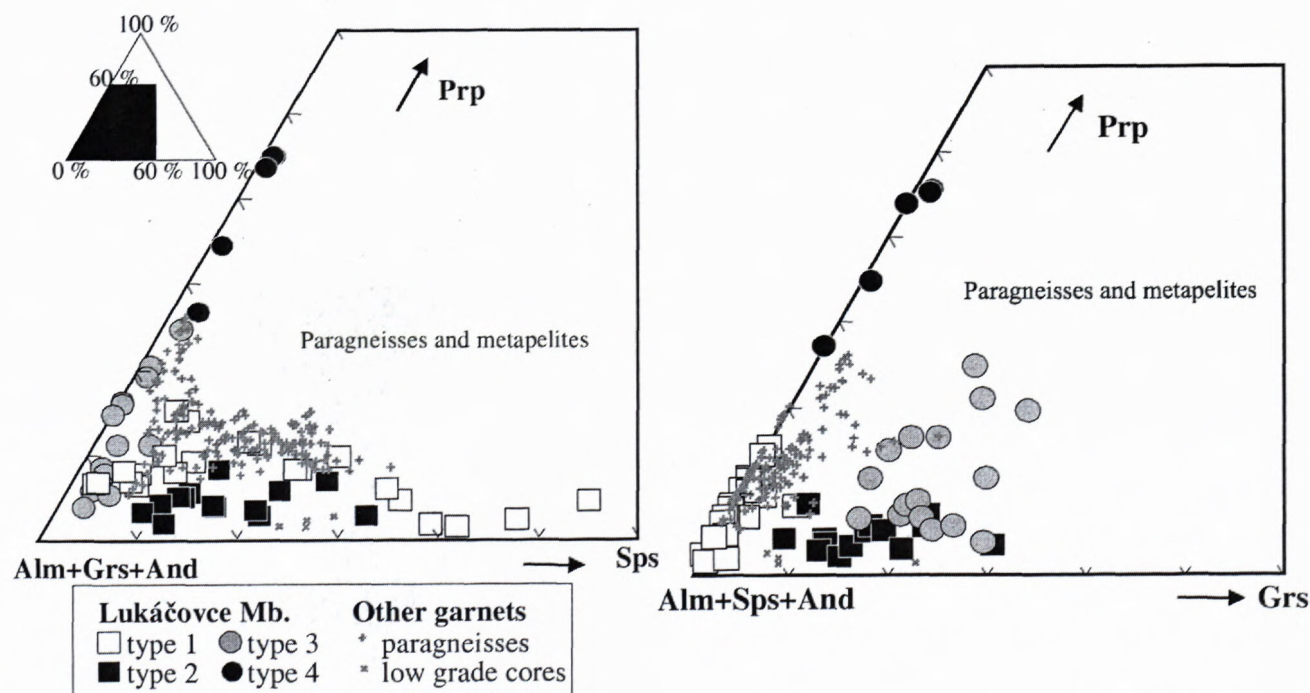


Fig. 4. Comparison of garnets of the Lukáčovce Mb. and garnets from metapsammities and paragneisses (comparative analyses – Dyda, 1981, 1990, 2002; Hovorka et al., 1987; Méres and Hovorka, 1989; Faryad, 1990, 1995, 1996; Vozárová and Faryad, 1997; Vozárová – unpublished).

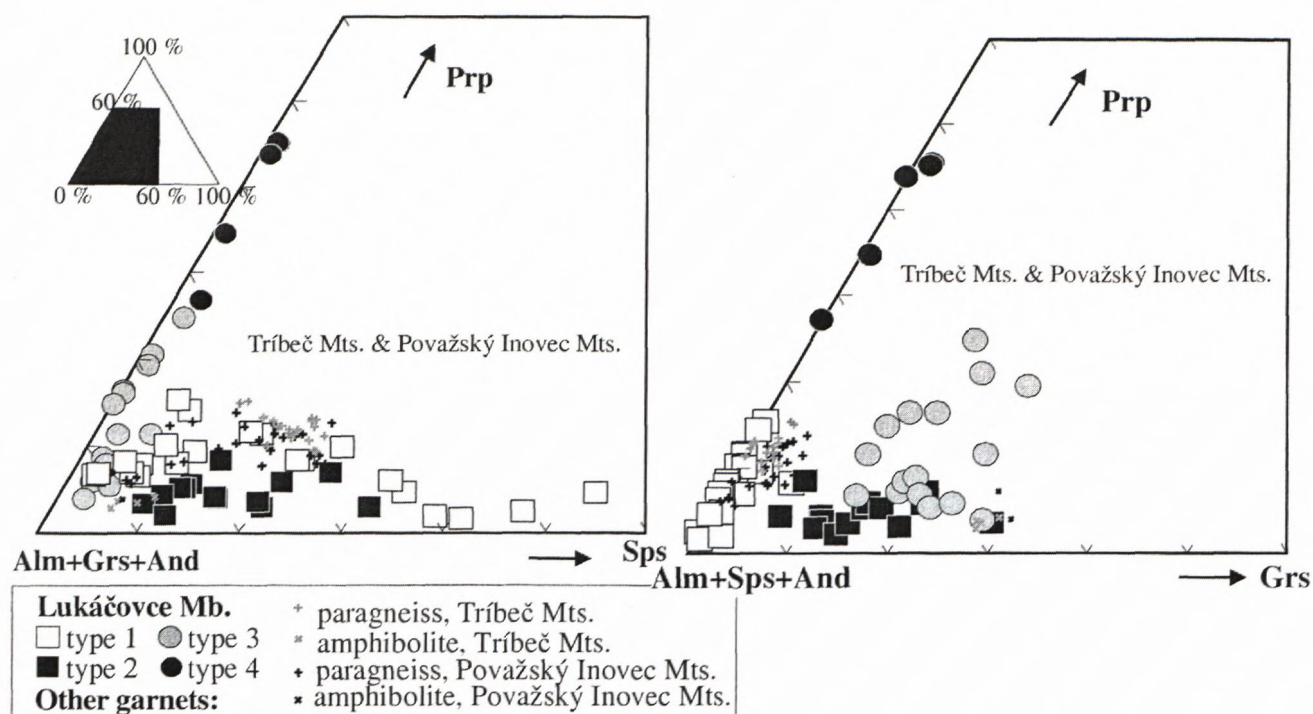


Fig. 5. Comparison of garnets of the Lukáčovce Mb. and garnets from crystalline complex of the Považský Inovec Mts. and Tríbeč Mts. (analyses of garnets from mountains – Hovorka and Méres, 1990; Zai'ko and Broska, 1996; Olšavský and Demko, 2005; Vozárová – unpublished).

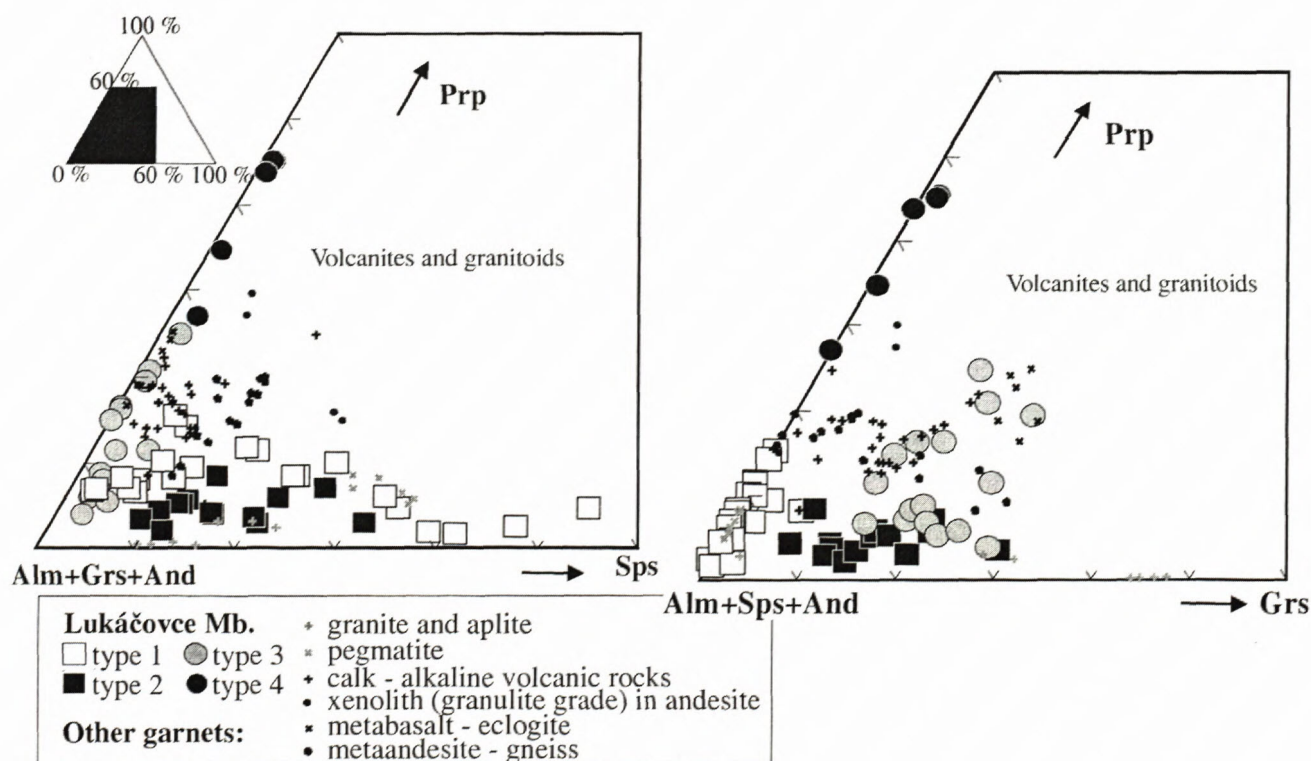


Fig. 6. Comparison of garnets of the Lukáčovce Mb. and garnets from neovolcanites and granitoids (analyses of garnets from granitoids – Dávidová, 1968; Petrík et al., 1995; analyses of garnets from neovolcanites – Zorkovský, 1956 in Kaličiak et al., 1988; Harangi et al., 2001; from metavolcanites: Faryad, 1990; Méres et al., 2000).

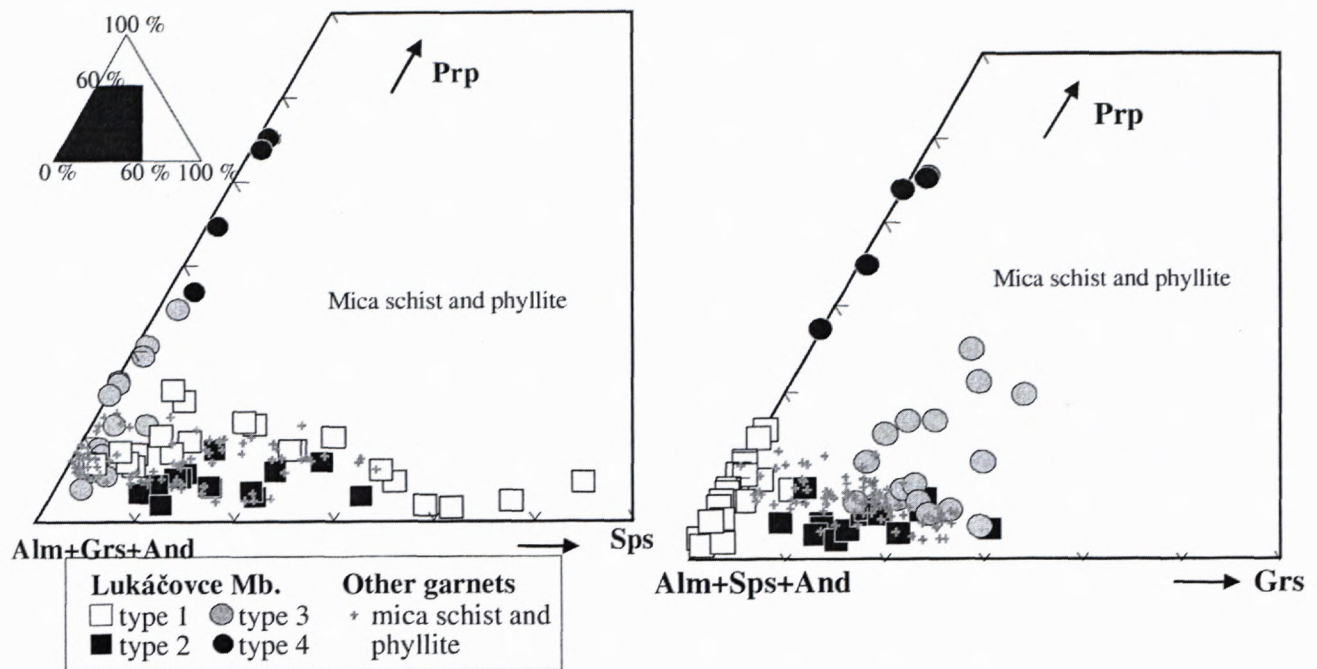


Fig. 7. Comparison of garnets of the Lukáčovce Mb. and garnets from mica schist and phyllites (comparative analyses: Vozárová – unpublished).

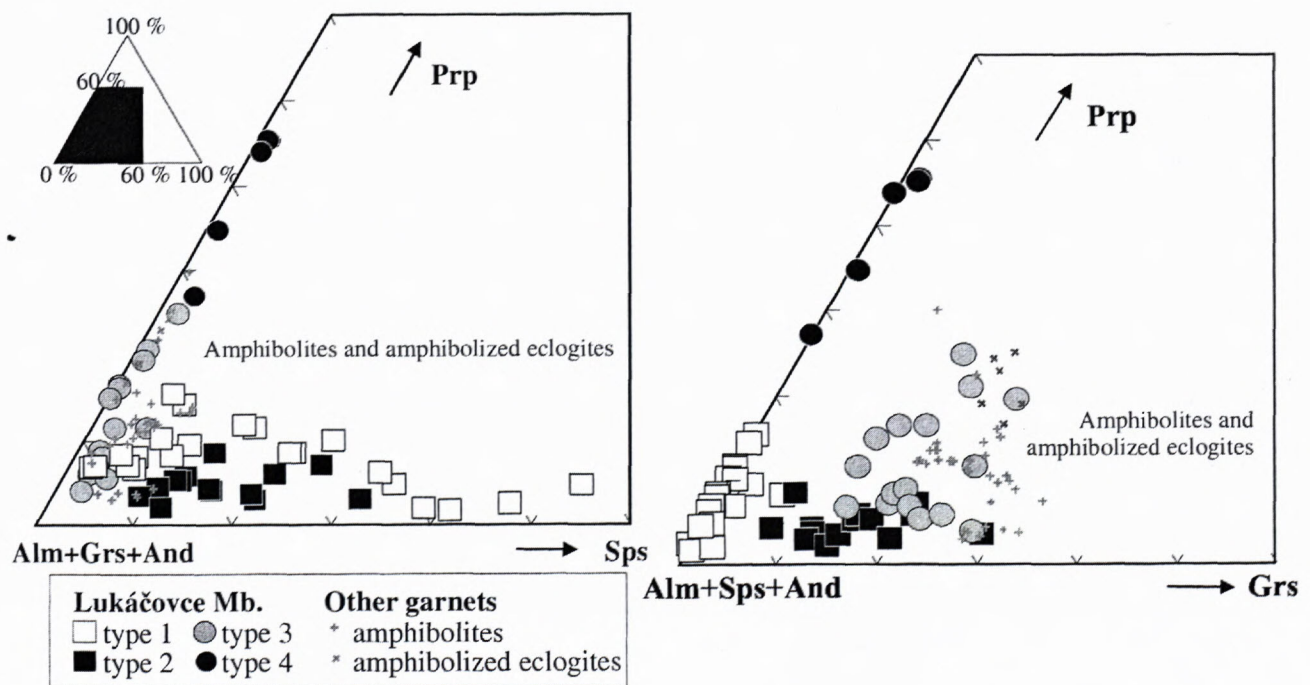


Fig. 8. Comparison of garnets of the Lukáčovce Mb. and garnets from amphibolites and amphibolized eclogites (comparative analyses – Spišiak and Hovorka, 1985; Hovorka and Méres, 1990; Faryad, 1995, 1996; Vozárová and Faryad, 1997; Méres et. al., 2000; Olšavský and Demko; 2005).

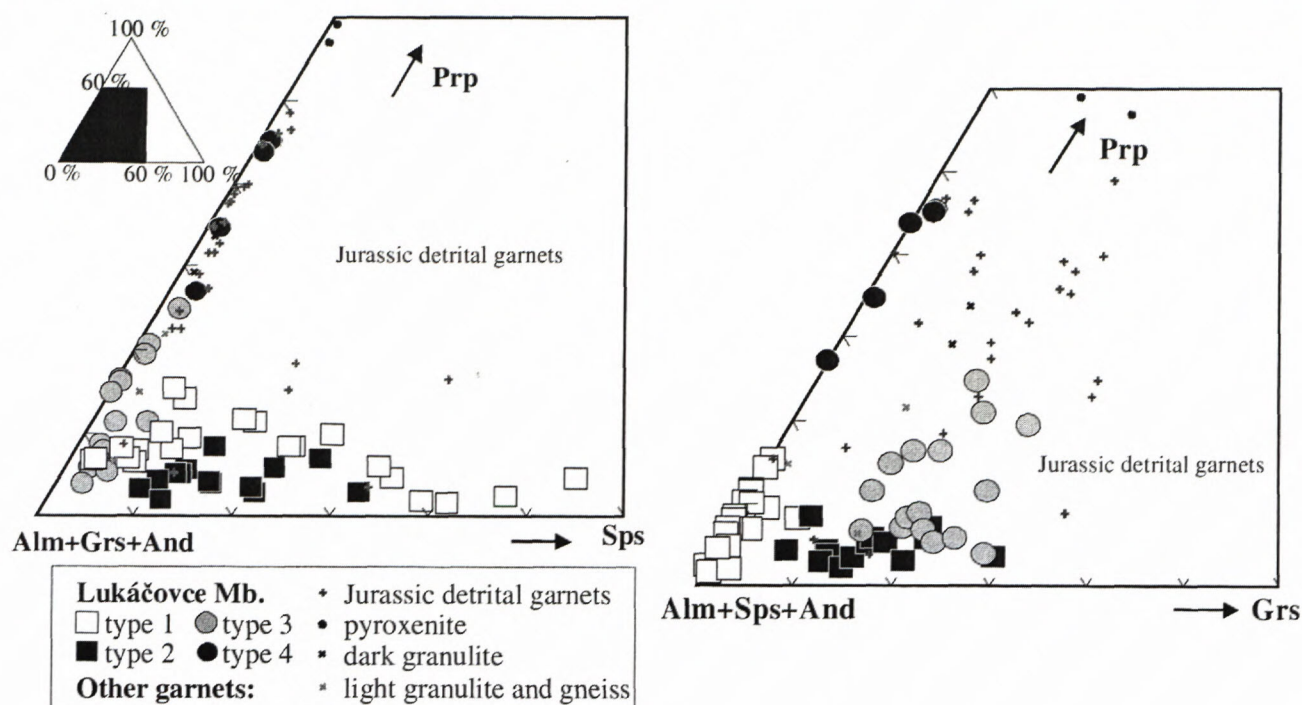


Fig. 9. Comparison of garnets of the Lukáčovce Mb., Jurassic detrital garnets and garnets from pyroxenites, light and dark granulites (comparative analyses: Jurassic garnets – Aubrecht and Méres, 2000; others – Dobretsov et al., 1984).

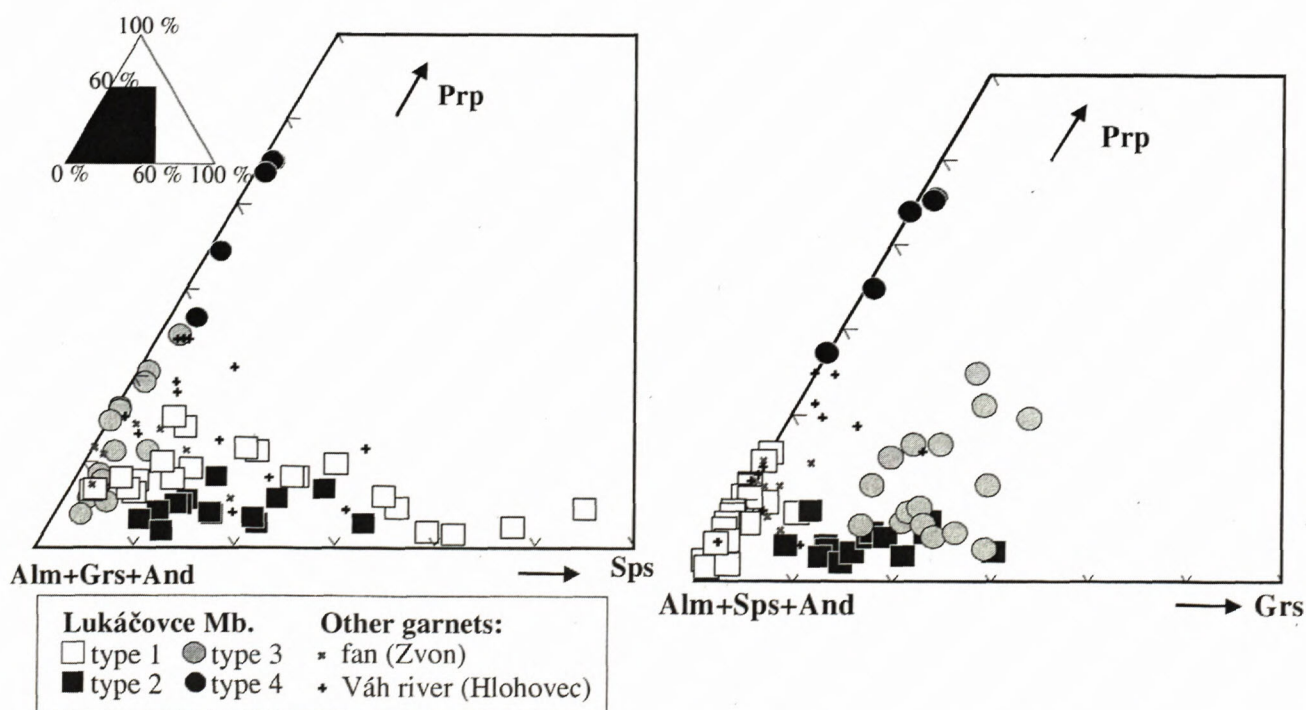


Fig. 10. Comparison of garnets of the Lukáčovce Mb. and garnets from Váh river (Würm) and alluvial fan from Považský Inovec Mts. (comparative analyses – Šarinová, 2004).

highly exceeded content of pyrope molecules in garnets from these paragneisses. Granulites are the only possible source, but such rocks until were not described in Slovakia. Only Aubrecht and Méres (2000) indicated similar values from Jurassic detrital garnets of the Klippen Belt and of the Central Carpathians (Fig. 9). They have set apart three big groups. First two groups represented garnets from the low grade and medium grade metamorphosed rocks, as phyllites, mica schists, gneisses and amphibolites. Third group included pyrope–almandine and pyrope–almandine–grossular garnets, whose source is still question under debate. Pyrope–almandine garnets should be originated from granulites, and pyrope–almandine–grossular garnets from eclogites. These authors stated as potential sources: 1) Moldanubian Zone of the Bohemian Massif; 2) exotic crustal segment (Sliezka cordillera); 3) high grade leptynite–amphibolite complex (LACWECA), to which authors (Hovorka and Méres, 1993) classified amphibolized eclogites of Branisko Mts. and Malá Fatra Mts., as well as complexes from Nízke Tatry Mts., Trábeč Mts., Veporicum and Gemericum. The present garnets from LACWECA do not reach demanded percent of pyrope molecules, and so LACWECA cannot be a primary source of pyrope–almandine garnets from the Lukáčovce Mb. Furthermore, minimal content of grossular molecules within the Lukáčovce Mb. garnets suggest their formation from granulites and not from eclogites.

With respect to presence of similar pyrope–almandine garnets at the Jurassic sedimentary rocks of the Klippen Belt and Central Carpathians (Aubrecht and Méres, 2000), there is possible to search their source in the Jurassic rocks from the cover, eventually nappe units of the Považský Inovec Mts. Fact, that during the time of the Lukáčovce Mb. sedimentation, there came into carbonates the weathering products is confirmed by the presence of silicified crinoidal carbonates debris and cryptocrystalline silicites with organogenic texture, often with pseudomorphoses after calcite and deformations (Šarinová, 2004). However, these mentioned garnets would have to be found straight in the Jurassic rocks of the Považský Inovec Mts. to confirm this theory.

Another potential source is represented with garnets with similar composition as the granulite facies xenoliths in neovolcanites (Fig. 6; Harangi et al., 2001). But this alternative is extreme unlikely. In that case garnets would have to be redeposited from xenoliths; and with supreme probability they would not reach needed percentage occurrence.

A possibility of transportation of such type garnets from the Klippen Belt area by rivers is practically excluded (low expectation to find such garnets; absence of such type garnets in the present deposits of the Váh river (Fig. 10); uplifted Považský Inovec Mts.). Naturally, it does not eliminate redeposition from older fillings of the basin. In this point maybe warns, that similar garnets were found at the flysch belt too (Otava et al., 1997, 1998 in Aubrecht and Méres, 2000). But these garnets still were not described in the Rišňovce depression. There is rather low probability, that the primary source of these garnets (granulites; metamorphosed rocks within granu-

lite facies) might have been found in the crystalline complex of the Považský Inovec Mts. or Trábeč Mts. Even if these granulite rocks were totally eroded, their presence ought to be manifested at least in the rounded pebbles material of the older Neogene or Paleogene basin fillings, what there does not happen until now.

Conclusion

Garnets of the Lukáčovce Mb. are derived dominantly from rocks of crystalline complex of the Považský Inovec Mts., namely from paragneisses and mica schists (types 1, 2 and 3). A portion of garnets could be alternatively originated from pegmatites (type 1) and neovolcanites (type 3). The source in pegmatites and neovolcanites is supported by the presence of the granitoid fragments within the gravel fraction. This source can be the primary one, or garnets can be redeposited from Neogene filling of the basin with other materials. The secondary source is likely for garnets from neovolcanites.

The source in amphibolites is not excluded (type 3). However, published analyses of garnets from leptynite–amphibolite complex from the Trábeč Mts. (Hovorka, Méres, 1990) are similar to garnets from the Lukáčovce Mb. only very marginally. Besides, composition of these garnets does not explain presence of pyrope–grossular–almandine garnets with contents of pyrope molecules 17–22 %. There were not described some amphibolized eclogites in the Považský Inovec Mts. up to the present time.

The primary source of pyrope–almandine garnets on the Slovak territory was not found until now. The presence of pyrope–almandine garnets in Jurassic carbonates of the Klippen Belt and Central Carpathians (Aubrecht and Méres, 2000) suggests potential source of these garnets type in Jurassic carbonates of the cover and nappes of the Považský Inovec Mts.

Although the primary source of pyrope–almandine garnets still remains undetected, presence of pyrope–almandine garnets is undeniable proved in the Quaternary sediments, and that contributes to extension of occurrence of such garnets in the Slovak territory.

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Revision of a mastodon find from the Neogene at Kuzmice near Topoľčany (Slovakia)

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Abstract: The study deals with the review of a mastodon find in Kuzmice (Slovakia). Schmidt determined the find as *Tetralophodon grandincisivus* and because of its well-preserved tusks and preserved remains of the skull it became a find of European importance. The age of the sediment was dated to the Late Pontian (Miocene). However, the revision of the material under study has shown that it is not possible to include the find in this genus. The find has clear characteristics, which are diagnostic for *Mammuth borsoni* Hays, 1834. Taking into account the fact and viewing new finds of mastodons from the locality, the age of the sedimentary complex is dated to the Late Pliocene (MN 16-17).

Key words: Pliocene, Slovakia, Kuzmice, Proboscidea, *Tetralophodon grandincisivus*, *Mammuth borsoni*

Introduction

A mastodon find at Kuzmice (Slovakia) was determined by Schmidt (1963) as *Tetralophodon grandincisivus* Schlesinger, 1917. The age of the sediment was dated to the Late Pontian (Miocene). Schlesinger's (1917) taxon "*Mastodon*" *grandincisivus* – allocated by Tobien (1978) to the elephantoid-genus *Stegotetrabelodon* – is classified as an amebelodontid indet. by Tassy (1985). This bunodont species spread from Maragha in Persia to the Central Europe (Osborn, 1936) where it is known at 5 localities (Austria – Mannersdorf near Angern, Paasdorf near Mistelbach; Hungary – Pestszentlőrinc, Neszmély and Slovakia – Topoľčany); (Schmidt, 1963). All localities from the Central Europe are dated to the Pontian (Miocene); (Schmidt, 1963). The discovery in Kuzmice was the sixth locality and it was the first find of this species with so well-preserved tusks and preserved remains of the skull (Schmidt, 1963). Because of this reason it became a find of European importance.

The revision of this specimen PZv – 23 enables to assign it to the species *Mammuth borsoni* Hays, 1834. This species belongs to zygodont trilophodont dibelodont longirostrine mastodons. Schlesinger (1922) derived this species from the Miocene species "*Mastodon tapiroides*" (= *Zygodont turicensis* Schinz, 1833) through the intermediate form *M. tapiroides (americanus)* divided into *M. borsoni*, *M. americanus* forma *praetypica* and *M. americanus* forma *typica*. They lived during the Upper Pliocene together with *M. borsoni*. At the end of that time they migrated to North America. The American mastodon had developed from European ancestors and migrated across the Bering pass to North America (Schlesinger, 1922). Lehman (1950) assumed that the American mastodon might evolved from zygodont mastodons existing on the American continent on the Miocene – Pliocene boundary. This might concern the genera *Serridentinus* or *Pliomastodon* (Lehman, 1950). Also Tobien (1976) assumed that *Mastodon americanus* Osborn, 1936 evolved from populations of zygodont mastodons parallelly to

Eurasian populations of *M. borsoni*. Molars of these mastodons are so similar that Tobien (1976) ranges them to one genus – *Mammuth*. This opinion may be accepted. Differences between the "species" *M. borsoni* and *M. americanus* forma *praetypica* cannot be regarded as species differences (Holec, 1985). It was already mentioned by Venjukov (1902) who found the characters differing two forms to one specimen. Schlesinger (1917) described the forms together from several localities of the former Austria-Hungary. Pavlová (1894) denoted the progressive form as *ohioticus* and the conservative form as *borsoni*.

During the evolution from *Zygodont turicensis* to *Mammuth borsoni* their lower tusks got reduced. *Zygodont turicensis* has normally developed lower tusks but those of *Mammuth borsoni* are markedly reduced, rudimentary (Holec, 1985). Although it is proved that mastodons, especially *Zygodont turicensis*, were forest animals, we must admit that with respect to the vast area that they lived in, they could not be restricted to one biotope. Mainly terminal types of mastodons *Anancus arvernensis*, *Mammuth borsoni* and its relative from the American continent – *Mammuth americanus* might also lived in steppe-forest, partly in arid environment (in contrast to *Deinotherium*) because they lasted up to the Pleistocene, and *M. americanus* even to the Holocene (Holec, 1985).

The remains of the species *Mammuth borsoni* are known from many European and Asian localities (Holec, 1985). In Slovakia, the species is known from Hajnáčka (Fejfar, 1961, 1964; Holec in Sabol (ed.), 2005), Strekov, (Schmidt AND Halouzka, 1970; Holec, 1996), Spišské Podhradie (Holec, 1992), Nová Vieska (Holec, 1996), Moravský Ján (Holec, 1986), Veľké Bielice (Holec, 1979), and Ceroviny (Holec et al., 2002).

The object of this work is a redetermination of the find and to disprove its dating to the Miocene. Schmidt (1963) has not described some structures in details. Therefore I considered necessary to make a revision and to describe this undescribed structures of the find.

Dental nomenclature was used according to Shoshany and Tassy (1996). Measurements were taken according to Göhlich (1998; modified) and Berta (1988; modified).

Geological settings

The fossil material described in this paper comes from a locality in the western Slovakia. It lies in the Nitra Upland in the district Topolčany. The Nitra Upland comprises the most extensive, northernmost offshoot of the Danube Lowland and it belongs to areally extensive regions. It extends by its southern part into the Danube Basin, its middle and northern parts are wedging in a form of wide bay among the Považský Inovec Mts., Trábeč Mts. and Strážovské vrchy Mts. It is separated from the Horná Nitra Depression by Uhrec brana gate. The upland is bound to the Považský Inovec Mts. and Trábeč Mts. by striking faults. The northern and north-eastern boundary to the Strážovské vrchy Mts. has an erosion-denudation character and as the only locally it has fault character with striking wedging into the mountains. The Nitra Upland is predominantly composed of Neogene deposits prevalingly covered by Quaternary deposits (Pristaš et al., 2000).

The locality is situated approximately 500 m, on the south-east from the road going from Kuzmice to Jacovce, on the field "Hájik". The locality is 289 meters above the sea level. The mastodon remains were found in overturned position in a sand pit (Schmidt, 1963). The find was situated in a stratum of grey-yellow, rustily spotted sand approximately 5 meters below where alternated sands of different granularity show a cross stratification (Schmidt, 1963). The organic remains are rare. The sedimentation took place in freshwater environment (Schmidt, 1963). As for the map and the profile of the locality, see Schmidt (1963, Fig. 1 and 2). As for the age of the locality, see discussion.

Methods

The material is housed in the Tribeč Museum. Photographs were made by camera Sony 101. Measurements were taken by tape measure and calliper rule. Abbreviations used in figures are as follows: I2 sin. – the left tusk, tad – trace of *alveola dentale*, fM2 – fang of M2 sin, M3 sin – left upper molar, m – maxilla, fo – *foramen opticum*, f – frontal, l – lacrimal, sqt – *squama temporalis*.

Systematic part

Class: Mammalia LINNAEUS, 1758
Group: Proboscidea ILLIGER, 1811
Suborder: Elephantiformes TASSY, 1988
Superfamily: Elephantoidae GRAY, 1821
Family: Mastodontidae HAY, 1922
Genus: Mammot BLUMENBACH, 1799
Species: *Mammot borsoni* HAYS, 1834

Synonyms:

1834 *Mammot borsoni* (Hays p. 334)
1963 *Tetralophodon grandincisivus* (Schmidt p. 169–174)
1985 *Tetralophodon grandincisivus* (Holec p. 32)
2000 *Tetralophodon grandincisivus* (Pristaš et al. p. 116)

Holotyp: M3 described by Hays, 1834, page 334.

Diagnosis: Species of *Mammot borsoni* is zygodont brevisrostrous trilophodont dibelodont mastodon. The tusks are long, relatively direct. Total length of the tooth M3 is usually 150 – 167 mm and maximum width of M3 is about 96 mm. Dentin thickness is about 5 mm.

Locality: Kuzmice (Slovakia)

Stratigraphic range: Pliocene, Mammal zone MN 16 - 17

Material: The remains of the skull of *Mammot borsoni* are significantly damaged and shapes of bones are not clear. The left side is relatively preserved, remained in fragments. The find is deposited as PZv-23 with the registration number 218/62 in Tribeč Museum in Topolčany (Slovakia).

Description

The structures of the skull or bones, which are missing in Schmidt (1963), are described in this part. It states also the new description of the teeth and the measurements of skull, teeth and tusks.

Skull

The total length of the find is 3350 mm. The maximum breadth of the find is 600 mm and maximum height is 410 mm above the molar. The length of the skeleton part is 1155 mm.

Maxilla: The left maxilla is preserved with M3 sin. and the fang of M2 sin. The surface of the bone is smooth. A part of maxillary *processus zygomaticus* sin. is preserved on the left part, standing out on the place of M3 sin. in ventral view. It juts out in postero-lateral direction. Its dorsal margin is a part of the ventral edge of the orbit. The distance between alveolus M3 sin. and the dorsal margin of *processus zygomaticus* sin. is 190 mm.

Two low depressions are preserved in the frontal part behind the line of the beginning of the tusks. The depressions have an oval concave shape, prolonged in antero-posterior direction. The surface is smooth. The left one is well preserved (Fig. 1a). It measures 230 mm in antero-posterior direction and 88 mm in medio-lateral direction. I consider them to be the traces of alveoli remaining from dropped older teeth, which were pushed away by permanent teeth. Therefore this area is shallow and significantly pushed at the anterior end. Its posterior part is bordered by the *pars molaris* of permanent teeth. Because of the pushing of teeth the inner part of the palatine shows naturally apparent deformation starting from the lingual margin of the area – as if it was a plastic tearing in the direction of the line of pushing. That caused the creating of structures, the orientation of which is similar to tectonic cuts. They are more noticeable on the posterior part close to the margin of the area. They rotate askew in acute angle towards the line of movement, to the lateral part. The structures end up in medial direction and the slope descends.

The preserved *processus palatinus* dext. et sin. is divided by *sutura palatina mediana*. It measures 490 mm in antero-posterior direction.

Frontal: A part of frontal is preserved in the left side. There is the dorsal margin of the left orbit, which is only partly preserved (Fig. 1b). It forms the dorsal edge of the interior smooth concave area, which continues in medial



Fig. 1. *Mammut borsoni* Hays, 1834: a – dorsal view on the left trace of alveola dentale. (Photo by M. Žáček); b – posterior part with dorsal interior part of orbit. (Photo by M. Žáček); c – frontal view (Tribeč Museum archives); 1 unit equals to 5 cm.

direction. The preserved part of the concave area measures 200 mm in antero-posterior direction. *Processus zygomaticus* of frontal is not clear and has never been linked with *os zygomaticum*. *Foramen opticum* is situated inside of this central area. The bordering part of the bone between *foramen opticum* and *fossa saci lacrimalis* is

broken. *Foramen opticum* has an ellipsoid shape for this reason. It measures 86 mm in dorso-ventral direction and 125 mm antero-posterior direction. Outside of the orbit, the frontal is not so complete and the rest of the bone is lost. Probably *squama frontalis* is partly preserved under the remains of the skull.

Lacrima: A part of lacrimal is preserved in the left side and forms the antero-medial margin of the orbit (Fig. 1b). The surface of the bone is smooth and the border with frontal is not clear.

Temporal: A part of temporal is preserved in posterior part of the left side (Fig. 1b). The bone is plane, gently convex of shape. The ventral part is lost, but the bone was probably longer than it is wide. The surface of the bone is smooth. *Processus zygomaticus* of temporal is preserved in its anterior part and juts out in antero-ventral direction.

Teeth

M2 sin.: The only fang of the tooth remained (Fig. 2). It is distinctly bare on lingual side. It consists of three fangs. Two fangs are well preserved however the third one is damaged. The fangs preserved at the lingual side measure 83 mm in length. The height of the bare part on the first one is 55.5 mm; the second one measures 59 mm in length and the third one measures 26 mm. The alveolus is seriously damaged on the buccal side, however the view from above renders visible the contours of all three damaged fangs on this side. The area of the fang measures 90 mm in breadth. The whole area is damaged but according to the number of three fangs from not preserved ridges, it is evident that the tooth had three yokes. The mark is called trilophodontism (as for this mark, see Falconer, 1857).



Fig. 2. *Mammut borsoni* Hays, 1834: naked fang of M² sin. (Photo by M. Žáčik); 1 unit equals to 1 cm.

M3 sin.: In general well preserved, the last ridge a bit damaged in the distal part. The tooth has four ridges (Fig. 3). Crosswise the half-ridges show one line. Therefore the cones and ridges are arranged in a direct vertical line versus antero-posterior line of the crown.

There are sharp vales between the ridges; they are not covered in profile. The vales are bit broader on the lingual side. The tooth does not tend to lay cement. The ridges are sharp, it is caused by anterior-posterior compression; transforming of central cones to sharp pretrite and postrite ridges is developed. The crown colour is light, greyish-blue. The tooth is apparently abraded. The

abrasion fades out towards the distal end. The buccal half-ridges are higher than lingual ones, while it is vice versa in last one. The lingual walls of the ridges show higher inclination than the buccal ones, which are quite steep. The measurements of M3 sin. correspond to the range of *M. borsoni* (Tab. 1).

Tab. 1. Size of the tooth M³ a sin. [mm]

Lenght max.	Width max.		Dentin thickness	
158	104		5	
number of the ridge	1	2	3	4
width of the ridge	104	93	90	71
crown height on the lingual side	43	45	52	42
crown height on the buccal side	49	54	56	33

Proloph (the first ridge) shows visible abrasion. The lingual half-ridge is damaged in the area of median sulcus. The ridge surface is immensely abraded. Naked dentin is on the main tips. Paracone has a form of a crater on the buccal side. There is a cleft in the area of the first vale on the tooth. The first lingual half ridge is subtly shifted. It was turned slightly counter clockwise in the view from inside. However, it is caused by preservation process. Protocone is significantly abraded. Metaloph (the second ridge) is abraded, especially the lingual part with naked dentin. Hypocone is a crater in the shape. There is a cleft on the lingual side of the second vale. Talon: triloph (the third ridge) is not much abraded, the dentin is covered. The fourth ridge is damaged in the distal part. Mostly, the lingual half ridge is damaged. Its posterior as well as the upper part of tip is missing.

The surface of the tooth is covered with small tuberosities. They are polished with the tongue on the lingual side so the surface of this part is more or less smooth. The mesial part of the tooth is preserved and well bounded. The cingulum protruded in this part. Its highest point of the area of median sulcus, reaching the height of 25 mm. Cingulum also in the shape of tuberosities runs through the buccal side and loops the first half-ridge up to the height of 18 mm. It passes through the exoflexus then it suddenly disappears.

Dentes incisivi: The tusks are long (Tab. 2.), relatively direct. The span between the tusks is approximately 330 mm at the beginning of alveoli. The tusks are crossed in the distance of 340 mm from the end of tips of I2 sin. and I2 dext. (Fig. 1c). The crossing is only secondary and is caused by post mortal and fossilization process. I2 sin. is slightly sagged down in the distance of 750 mm from alveolus (in the position as it was discovered). That curving also resulted in not much apparent medio-lateral fissures extending on almost entire breadth of the tusk within the distance from 640 to 1080 mm. The entire tusk is unnaturally anchored in the alveolus. It is slightly shifted towards the interior part so the tusk I2 sin. is directed below I2 dext. (due to overturned position nowadays). During the life of animal, there was not the crossing. I2 dext. is approximately in correct position from anatomical aspect.

Tab. 2. Size of tusks [mm].

The size of I ² dext. [mm]	length in the exterior part	2240
	length in the interior part	2140
	length from the upper side	2220
The size of I ² sin. [mm]	length in the exterior part	2320
	length in the interior part	2180
	length from the upper side	It is not possible to measure because of crossing

Discussion

The restudy of the material PZv – 23 enables to assign it to the species *M. borsoni*. It is not possible to regard the preserved molar M3 sin. as bunodont type. It has typical zygodont morphology. Schmidt (1963) stated that the preserved molar had likely five and half ridges, while the first and the second ridge was not preserved. However, the almost entire tooth remained and the mesial end shows normal ending. It has four ridges. It is possible that Schmidt (1963) considered the fang of M2 sin. to be the remaining part of the first and second ridge.

According to presented results this is a zygodont mastodon *Mammot borsoni* Hays, 1834. The find of mastodon from Kuzmice is redetermined for these marks:

1. Zygodont tooth M3 sin., crosswise the half-ridges show one line, there are sharp vales between the four ridges and they are not covered in profile. It is typical mark for this species (Fejfar, 1964) and it is a key determination characteristic because it is not possible to find it in bunodont types. It is typical for zygodont types (Fejfar, 1964; Holec, 1985).

2. The lingual walls of the ridges show higher inclination than the buccal ones, which are quite steep. This typical mark is described for zygodont mastodons (Tobien, 1975).

3. Metric of M3 sin. corresponds to *M. borsoni* (Tab. 1) (Osborn, 1936; in comparison with material in Holec, 1985).

4. Trilophodontism is a typical mark for zygodont mastodons (Falconer, 1857), which never reached the tetralophodontic level of bunodont types (Tobien, 1973).

5. The tusks are long (Tab. 2), relatively direct, that is a typical mark for genus *Mammot* (Tobien, 1975).

For the remarks it is not possible to regard this find as taxon *grandincisivus* Schlesinger, 1917. The find has not progressive characters.

Schmidt (1963) quoted there are sediments from Upper Pontian (Upper Miocene) in the subsoil of covering formations from Quaternary period in the excavation as well as in the broader area. The revision and examination of new finds of teeth disprove dating as Miocene. Pristaš et al. (2000) has classified the sediments as Volkovce Formation (Pliocene – Dacian). The species *Mammot borsoni* Hays, 1834 indicates mammal zone MN 16-17 (Pliocene, Dacian-Romanian); (Holec, et al., 2002). Another finds of not published mastodons also

come from this locality: namely the tusks and teeth of the species *Mammot borsoni* Hays, 1834 – m3 sin. (PZv-22) and *Anancus arvernensis* Croizet et Jobert, 1828 – m3 dext. (PZv-36), m3 sin. (PZv-36b, PZv-18b). Similarly alternation of half ridges on M3 of Kuzmice findings in *Anancus arvernensis* proves up to Pliocene. If we see the evolution line starting from *Gomphotherium* genus, *Tetralophodon* up to *Anancus* genus we may find out that the alternation of half-ridge moves from milk teeth to permanent teeth. A slight shift of half-ridges on D4 and M1 is seen in typical form of *Tetralophodon longirostris* from Early Pannonian. The alternation of half-ridges on D4, M1, and M2 is regular; the same is variable on M3 in interim form of *T. longirostris* and *A. arvernensis* from Middle and Late Pannonian. Eventually the alternation of half-ridges on M3 is also fully developed in typical form of *A. arvernensis* from the end of Pliocene (Holec, 1985); the alternation on M3 is distinct in Kuzmice finds. The other progressive characteristics, for instance the tendency to lay cementum that is developed on some teeth (mainly m3 sin. PZv-18b) also proves the age of Pliocene (this progressive mark is characteristic for Late Pliocene – as for progressive marks, see Holec, 1985). The trend of laying cement is not clearly developed in many teeth of *A. arvernensis* from the locality but in other finds that is already developed. It proves a certain diversity of population and different manifestation of progressive characteristics (intraspecies variability).

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Influence of extreme climatic conditions upon landslides development in the Slovak Republic

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Abstract: The paper demonstrates that the analysis of rainfall data allows to predict landslides occurrence within certain regions of Slovakia. For definition of relation between climatic conditions and groundwater table level in slopes a method of cumulative line of effective precipitation has proven to be competent. Based upon knowledge of daily effective precipitations intensity and groundwater table fluctuations it is possible to predict the groundwater level rising and, if measuring data on landslide activity are at hand, it is possible to predict future development of any landslide.

Key words: landslides, effective precipitation, snow melting, groundwater table regime

1. Introduction

From the observations of slope movements initiation it follows that very frequently a short-term process of intense subsurface infiltration of precipitation waters is a crucial (triggering) factor. Consequently, the infiltrated water partially supplies humidity in the zone of aeration and in the case of full saturation it may result in groundwater level rise. As a source of infiltrated water there may serve rain precipitation, however, very important there is snow melting process, mainly in the case of quick process. Based upon available data (inquiry, SHMI) this paper points out the regional influence of relatively short-term climatic events upon landslides evolution:

- intense precipitation in July 1997 and other summer periods
- snow melting and precipitation in March and April 2000.

2. Method of cumulative line of effective daily precipitation

In order to analyse the relation between fluctuations of the groundwater level and rainfall intensity, or the quantity of water released by melting snow, there has been adopted the method of cumulative line of the effective potential amount of water daily precipitation. Under the term effective precipitation we understand the maximum potential amount of water that can infiltrate the ground. The part of the rainfall that flows off as surface runoff or is intercepted by plants is disregarded.

The estimation of effective rainfall is based on subtracting the evapotranspiration value from the falling rainfall value:

$$Z_{ef} = Z - ET_{pot} \text{ [mm]}, \quad (1)$$

where:

Z_{ef} – effective precipitation,

Z – precipitation fallen,

ET_{pot} – potential evapotranspiration.

Daily values of the potential evapotranspiration ET_{pot} were calculated according the formula by Haude (in Hölting, 1996).

From the relation (1) it follows, that the effective precipitation during rainless periods manifests a negative value because of evapotranspiration. During this period there does not occur infiltration into the rock environment; on the contrary, the humidity is released from the soil.

For periods when the infiltration of rainfall into a rock environment occurs or humidity is released, a method to determine the cumulative line of daily effective rainfall (positive and negative values) was applied. The rising sections represent periods with infiltration of the rainfall; the downward ones indicate the release of the humidity from the rock environment. The horizontal parts of the line evidence for a balance between rainfall and evapotranspiration; the effective rainfall is equal to zero.

The course of this cumulative line may almost truly reflect the fluctuation of dominantly shallow groundwater level horizons, which is depicted in Fig. 1.

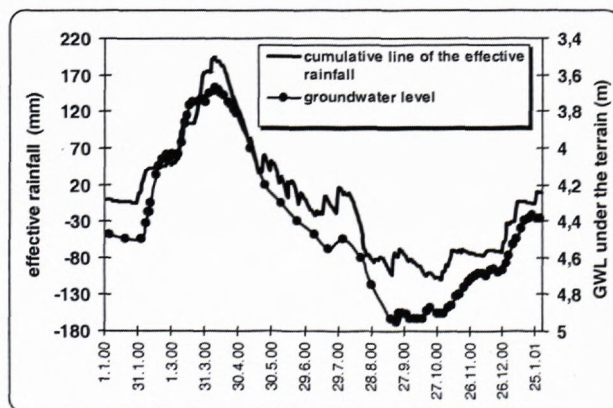


Fig. 1. Dependence between groundwater level fluctuation and the cumulative line of the effective rainfall

It is relatively easy to acquire values of the effective precipitation during the summer period according to the formula (1). However, during the winter period the situa-

tion is far more complicated. During the rainless cold period with daily air temperatures ranging around 0 °C and less, we may calculate with evapotranspiration from the snow surface. According to Rachner (1987) the daily evapotranspiration from temporary winter snow cover is estimated in January above 0.1 mm and in March up to 0.2 mm. The fallen precipitation in form of snow is not calculated as the effective one, only its equivalent corresponding the melting.

There is possible to define the water amount in mm released from melting snow according to the formula:

$$h = h_s \times s \text{ [mm]}, \quad (2)$$

where:

h_s is snow cover height [mm],

s is water equivalent of snow cover – WESC.

However there is necessary to define the snow cover thickness and water equivalent of snow cover (WESC). The WESC is not measured daily at majority of climatic stations; generally it is measured only once a week. Therefore it is inevitable to distribute evenly the weekly effective precipitation from melting snow according number of days between separate WESC measurements. Even more complicated there is determination of effective precipitation, when mutual snow melting and rainfall occur and the evapotranspiration has to be taken into calculation.

Only this complex way calculated daily effective precipitation allows us to construct **cumulative line** and to adopt it to analyse climatic conditions influence upon the groundwater level regime and, consequently, upon the slope stability.

3. Landslides in Slovakia triggered by intense rainfall in July 1997 and in further summer periods

July 1997 has become known thanks to floods, which were concentrated in the NW Slovak regions, prevalently. Since 1881 this was the second richest July in rainfall on the Slovak territory (Faško et. al., 1997). The most intense period recorded was 5th to 9th July, when within 5 days there fell up to 192 mm of rain.

The intense rainfall in SR triggered numerous landslides. In general, these were relatively shallow landslides, evolved in deluvial sediments, which use to happen during intense rainfall in tropical regions. However, these landslides did not occur only within the areas susceptible to sliding (reactivation of older landslides), but also on so far "safe slopes". The same situation in more accentuated form was observed in the Flysch Belt in Moravia (Marschalko, 2002).

In the area of Ľubovnianska vrchovina Upland (Flysch Zone) there occurred extensive planar shallow landslides in July in 1997 and 2001 as well as in 2004.

To analyse the rainfall in this region there was depicted a course of cumulative lines of the effective precipitation (method from the Chapter 2) from months May to July within years 1997-2005 from the Plaveč rain-gauge station (Fig. 2).

The daily effective precipitations, which were the triggering mechanism of landslides, reached on July 8, 1997

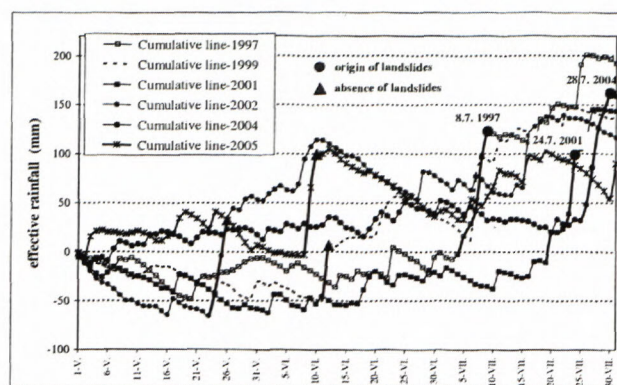


Fig. 2. Cumulative lines of the effective precipitation for the months of May-July for 1997-2005 from the Plaveč rain-gauge station.

- 54.5 mm, on July 24, 2001 – 60.2 mm and on July 28, 2004 – 50.16 mm. Almost the same amount of effective precipitation was recorded also in 1999 and even twice – June 12, 1999 – 55.32 mm and July 7, 1999 remarkable 66.22 mm. The landslides did not occur in further days with intense precipitation (July 16, 2002, June 9, 2005 - daily cumulative amounts 68,9 mm!). From the above it is obvious that the single daily effective precipitations, although of intense character, were not an immediate cause for landslides development.

However, the analysis of effective precipitation in days preceding the landslides development indicated a variable state of rock massif saturation. The Tab. 1 depicts the sum of the effective precipitation preceding the days with intense effective precipitation.

From the data in the Tab. 1 it follows, that the sum of the effective precipitation preceding intense precipitation (5 and 10 days) recorded on June 12, 1999, July 7, 1999, July 16, 2002 and June 9, 2005 shows a negative value. This means that there prevailed evapotranspiration above rainfall and it was released humidity from the near-surface parts of the rock environment. Therefore a part of intense precipitation only supplemented the missing humidity. On the contrary, the positive values of the effective precipitation sum before intense precipitation (5 and 10 days) on July 8, 1997, July 24, 2001 and July 28, 2004 speak for relatively high saturation of the rock environment.

Based upon these analyses there is possible to state that the shallow landslides may occur in the Ľubovnianska vrchovina Upland, provided 5 days before effective precipitation, which sum exceeds 50 mm in one day (precipitation, which triggered the landslide), the sum of effective precipitation is higher than 45 mm.

4. Influence of the effective rainfall and melt-water from snow upon the groundwater table fluctuation at the landslide site Bánoš

The landslide evolved in spring 1999 on the southern slopes of the altitudinal point Bánoš near Banská Bystrica, Central Slovakia, within the Tertiary sediments (Kopecký and Ilkanič, 2001). There was analysed at this site the influence of so-called effective rainfall and the effect of water originating from melting snow, upon the ground-

Tab. 1. Cumulative lines of effective precipitation for months May-July in the years 1997- 2005 from the Plaveč station.

	8. 7. 1997	12. 6. 1999	6. 7. 1999	24. 7. 2001	16. 7. 2002	28. 7. 2004	9. 6. 2005
Effective precipitation on very date of event (mm)	54.47	55.32	66.46	60.22	53.10	50.16	68.90
Sum of effective precipitation 5 days before the event (mm)	46.77	-8.70	-21.92	47.86	4.65	47.39	-1.60
Sum of effective precipitation 10 before the event (mm)	51.42	-17.56	-39.13	60.67	-3.76	48.04	12.60

water table variations. For this analysis there were used the groundwater table measurements from the nearby area, which preceded the slide development.

It has been shown that using the suggested method of cumulative line of the effective precipitation there is possible to correlate relatively well the relation between the effective precipitation (rainfall and water from melting snow) and groundwater table fluctuation.

Provided there are at hand measurements of groundwater table at any site, it is possible based upon data on the groundwater table rise and intensity of the effective precipitation to construct a correlation diagram (Fig. 3), which can serve together with relevant climatic data for groundwater table fluctuation modeling.

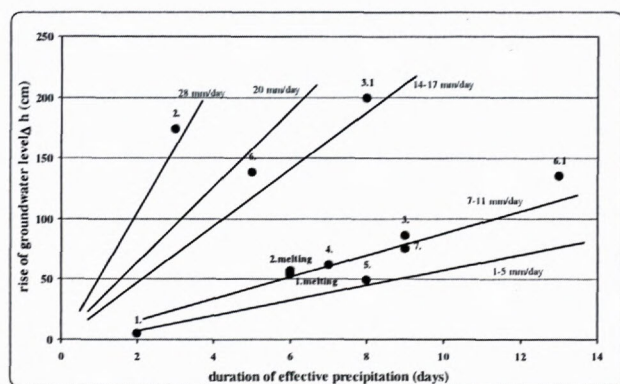


Fig. 3. Dependence of groundwater level rise upon the period duration of effective precipitations and their intensity (locality Bános).

This way we can define also state of stress in the slope and the conditions under which the slope failure occurred. The stability calculations at the Bános site have shown that the maximum value of the groundwater table, at which the slide evolved, is almost identical with the groundwater table acquired by modeling with the values of the effective precipitation.

It is necessary to point out that the accuracy of correlation diagrams depends upon frequency of relevant data collection. This is valid for the effective precipitation intensity, mainly.

We have also to point out that the method of the cumulative line can be applied mainly for near-surface groundwater table horizons, where the groundwater table reacts upon the intensity of the effective precipitation with relatively short retardation. Than for deeper groundwater table horizons there is inevitable to determine influence of other factors, which transform incoming impulse from the effective precipitation.

5. Snow melting and intense precipitation in March to April 2000 in Slovakia

From the results of the inquiry (Kopecký, 2002) it follows, that the March to April 2000 was the further period when the major part of Slovakia was hit by landslides. Within this period the landslides were registered mainly in the Laborecká and Ondavská vrchovina uplands, in the Kysuce, Liptov and Orava regions.

The water value of snow cover and cumulative rainfall amounts could tell us a lot about the extreme state, which evolved due to combination of snow cover melting and intense precipitation.

Under the water equivalent of snow cover (WESC) we understand the water amount, which is accumulated in snow column (in mm of water column). In the Tab. 2 there are the data on the WESC occurrence probability and their up to now maximum identified values and comparison with the data from 2000.

Also these data show that during the winter 2000/2001 there was actually accumulated a noteworthy snow cover, which contained a significant water volume, which was released from the snow melting.

The Tab. 3 presents data on monthly precipitation totals in March 2000 from selected stations.

5.1 Landslides in flysch formations developed at the margin of the Chočské vrchy Mts.

The development of these landslides was studied in detail based upon the climatic data (precipitation, temperature, relative air humidity, snow cover thickness, WESC) from the stations Liptovská Mara, Liptovská Ondrášová and Bobrovec. In March 2000 there developed or were reactivated:

- 9 landslides in Kalameny
- large earthflow in Malatiná
- landslide in Leštiny, which threatened the building of local dairy
- landslide in Veterná Poruba and Jakubovany

The Fig. 4 illustrates the course of cumulative line of the daily effective precipitation from this period. Besides this it shows the true precipitation totals and effective precipitation, which is divided into effective precipitation from rain and effective precipitation from melting snow cover, whereas their determination was rather complicated as we have already stated in the Chapter 2 (precipitation type, temperature, snow cover thickness, WESC).

A steep slope of the cumulative line of the effective precipitation was caused in periods 2.2-7.2. and 22.3.-29.3.

Tab. 2. Data on the water content of the snow cover from selected climatic stations.

Station	WESC occurrence probability (mm) once per years					Max. value		year 2000	
	2	10	50	80	100				
Plaveč	52	104	151	165	172	135 mm	22. 2. 1963	126.0 mm	31. 1.
Oravská Lesná	171	318	452	490	509	396 mm	10. 3. 1956	401.6 mm	20. 3.
Huty	83	189	285	312	326	272 mm	10. 3. 1952	166.0 mm	20. 3.

Tab. 3. Monthly precipitation totals from selected stations in March 2000.

Station	Long-term mean valid for March (mm)	Precipitation total for March 2000 (mm)	% of long-term normal
Čadca	56.0	156.0	278
Liptovská Mara	32.6	89.3	273
Nižná Polianka	41.0	92.0	224

29.3. due to snow melting and within 8.3.-11. 3. 2000 due to rainfall. It is obvious that by "classical" depiction of real precipitation it would not be possible to grasp the influence of the melting snow upon groundwater supply. Here comes into action a retarded impact of snow precipitation during melting period; in classical scenarios this part of precipitation was taken into consideration at the very time of their fall out. We have also to mention that the snow cover height was not the same at all sites (various volumes of the effective precipitation from melting snow) and moreover, the snow melting did not occur at all places simultaneously, but it was retarded due to effect of the altitude and slope orientation.

The influence of the effective precipitation upon the groundwater table level fluctuation is assessed in the Chapter 4. In March 2000 at the Liptovská Mara landslide there were identified in some piezometric gauges the maximum levels since 27 years of observations. This fact could be also approximated to the extreme stress state of the groundwater table within the surroundings, with consequent slope stability decrease.

A fact that the precipitation affected also deeper-situated groundwater table resulted in development of landslides of slip-type with deeper slip planes (8-20 m).

The first snow melting (Fig. 4) occurred by the beginning of February and the released effective precipitation saturated the zone of aeration and partially caused the rise of groundwater table level. During March 8 and 9 there fell in total 37 mm of the effective precipitation, which resulted in immediate rise of the groundwater table, because the zone of aeration had been already saturated. During this phase there developed the landslides in Jakubovany and Leštiny. From March 22 till March 29 there occurred total melting-down of the snow cover and was released a notable amount of the effective precipitation (ca 70 mm). This snow thawing triggered the landslides development in Malatiná (Fig. 5), Veterná Poruba and Kalameny.

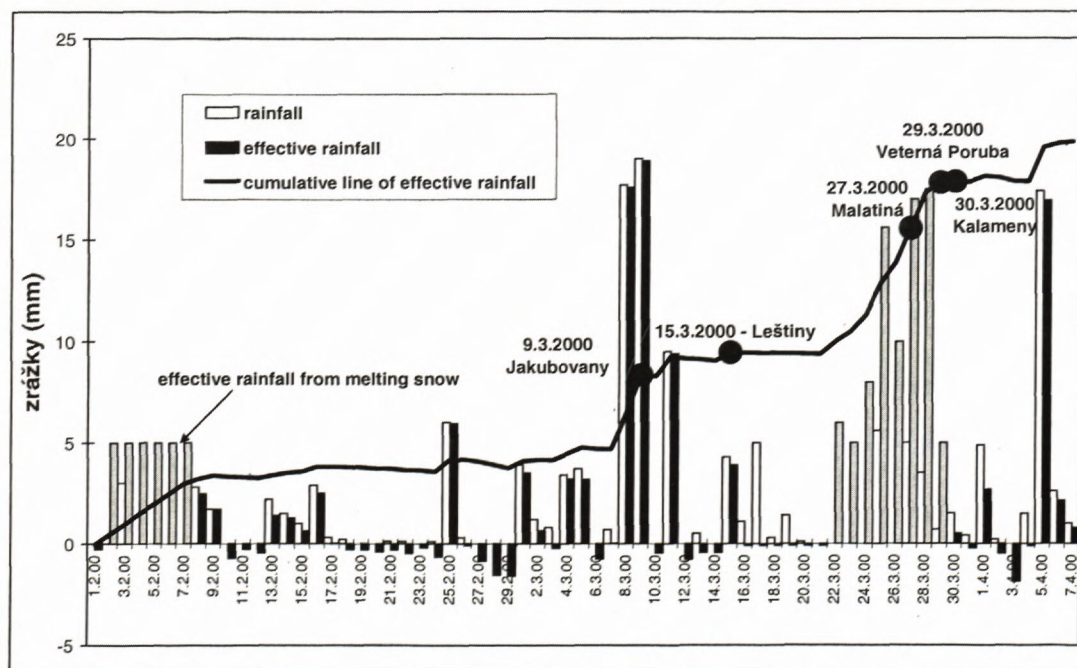


Fig. 4. Influence of the effective precipitation from rain and effective precipitation from melting snow upon the slope deformation evolution in spring 2000.

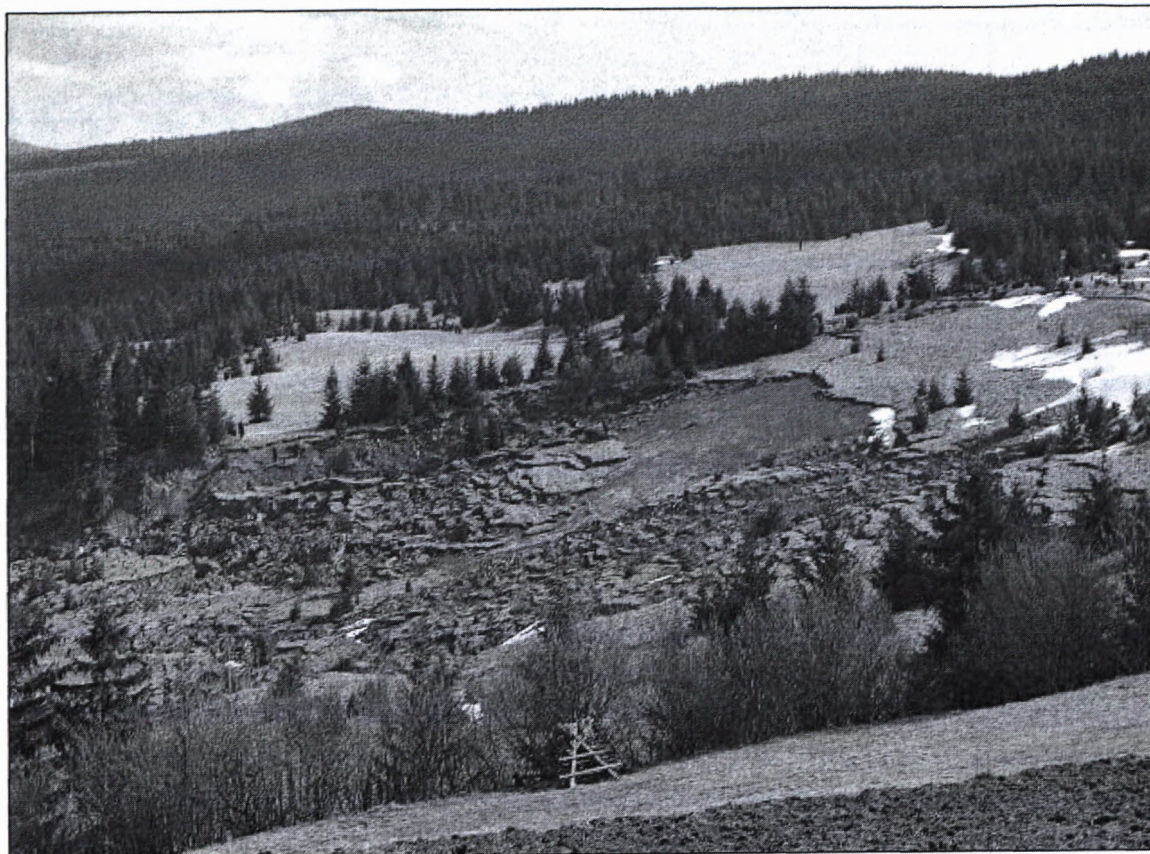


Fig. 5. Landslide near the Malatiná village (27. 3. 2000).



Fig. 6. Water-pipe in accumulation of landslide near Hrinova dam (April 2000).

5.2 Landslides developed in spring 2000 in other regions of Slovakia

On April 6, 2000 there evolved a landslide near the water treatment work – Water Reservoir Hriňová (Kopecký, 2003), which damaged an important group water pipeline supplying with potable water 60 000 inhabitants (Fig. 6). According to the data by SHMÚ (Slovak Hydrometeorological Institute) the monthly precipitation total in March within the area of interest equaled 112.7 mm, which corresponds to 298% of the long-term mean. At the same time it melted down by the beginning of the second decade of March the snow cover and water equivalent equaled to 70 mm.

By March/April it developed a landslide near Zázrivá, which destroyed a forest stand.

Based upon the information collected from various sources there were documented 56 cases of slope deformations throughout SR within this period.

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Determination of liquid limits of fine-grained soils

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Abstract: The paper presents the results of laboratory investigation for determination of the liquid limits using fall-cone method and method based on Casagrande type devices. The fall-cone method, which has not been used for liquid limit determination in Slovakia, should be adopted in Slovak laboratories according to the recommendations of Eurocode 7 and will become preferred method for determining the liquid limit of soil. Comparison between the results obtained by the use of these two methods and relationship between them are therefore very useful when both methods will be used for determination of liquid limits in geotechnical laboratories in Slovakia to assess the behaviour of fine grained soils and for their classification. Results are presented for soil samples from different localities around Slovakia with different liquid limits. The main differences between these two methods and laboratory test results with relationship between them are presented.

Keywords: liquid limits, Casagrande method, Fall cone method, Atterberg limits, consistency limits

1. Introduction

Consistency is important for description of a fine-grained soil state and the nature of the soil. Consistency limits, also called the Atterberg limits, comprise the liquid limit, plastic limit, and the shrinkage limit. These limits are named after Swedish chemist, who defined them at the beginning of 20th century. These limits depend on grading of soil (the size of the grains), on the nature of grains, i.e. on the mineralogy (the amount and the type of clay minerals) and they are also used to determine geotechnical properties and mechanical behaviour of fine-grained soils. Consistency of soil changes with the water content, from the liquid state through a plastic state up to firm, non-plastic state with fissures occurring at small deformations. The liquid limit represents the water content, at which the soil behaviour becomes liquid, or soil passes from liquid to plastic state. Two methods for liquid limit determination of fine-grained soils by laboratory tests are presented in this paper.

Fall-cone method is a preferred method for laboratory liquid limit determination according to Eurocode 7 Geotechnical design – Part 2 Ground investigation and testing. This standard should be implemented in members of European Union from 2010. This method has been developed and standardized in different countries (for instance in Canada, Japan, United Kingdom, Sweden, France) since that time. Slovak standard STN 72 1014, valid from 1968, defines two methods for liquid limit determination: Casagrande method and Vasiljev's method. The Vasiljev's method has been used in Russia and several former Soviet Union countries. Because of different construction of the cone and different mechanism of penetration it provides results, which are hardly comparable with other fall-cone tests. Almost all values of liquid limits in Slovakia have been determined by Casagrande method,

therefore it is very important to know the relationship of the fall-cone liquid limit with the Casagrande one. Fall cone method has been used more widely in Slovakia since 2004. This method had been used sporadically only for determination low plasticity soils before.

2. The fall cone method

The fall cone method is based on measurement of depth of penetration of fall cone into a specimen of the soil in the remoulded state with grains smaller than 0.5 mm. This method is based on standardized cone of certain weight penetrated into a soil. The cone must be able to fall freely and the penetration must be measured to certain (sufficiency) accuracy. Several types of fall-cones are used around the world. The differences between them are the angle of the cone, which could be 30° or 60°, its weight and the depth of penetration at which the liquid limit is determined.

The European Regional Technical Committee ETC 5 Laboratory Testing of the International Society for Soil Mechanics and Geotechnical Engineering (ISSMGE) was set up in 1991 to develop recommendations for performance of routine geotechnical laboratory testing, which included three methods for liquid limit determination (Farrell et al., 1995). Discussion on the choice of liquid limit determination methodology was the subject of 11th European conference ISSMGE ETC 5 Workshop (1995) in Copenhagen, Denmark. Swedes (Hansbo) and Danes preferred liquid limit determination by the Swedish fall-cone, which is the oldest method in Europe and has been used since 1915. ETC 5 realized a comparative study for liquid limit determination by the Swedish and the British fall-cone methods for soils with different w_L . Laboratory testing program of ETC 5 (Farrell et al., 1999) was also focused on repeatability and the operator sensitivity of

each fall-cone method. A method comparison study was performed in five European laboratories: TCD Ireland, BAW Germany, RGD Netherlands, SGI Sweden and BRE Great Britain. The results of 80 tests performed on soils with liquid limit from 20 % to 95 % were used and a regression curve with regression equation

$$w_{L\ 30^\circ/80\ g} = 0.998\ w_{L\ 60^\circ/60\ g} + 0.919$$

was obtained for comparison of 30°/80g a 60°/60g fall-cone method, which is shown in Fig. 1. This experimental study showed, that for geotechnical practice, both mentioned types of fall-cones give more or less equal values of liquid limit. These two types of fall-cones are specified also in technical specification of European committee for standardization CEN ISO/TC 17 892-12: 2005. This document will be proposed to be accepted as a European standard in the future and it is a reference document for EN 1997-2.

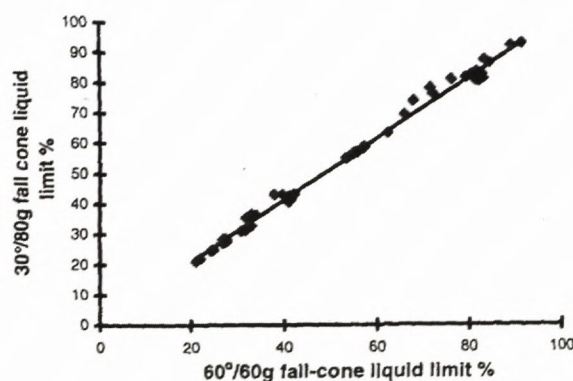


Fig. 1. Comparison of liquid limits determined by 30°/80 g and 60°/60g fall-cone (Farrell et al., 1999).

This European technical specification is not yet implemented as Slovak national standard. Eurocode 7 Part 2 recommends the use of two types of fall-cones: 60g/60° cone (the Swedish fall-cone) or 80g/30° cone (the British fall-cone). These fall-cones differ within very small and acceptable limits (Farrell, 1999; Leroueil, 1996). The main differences in cone penetration requirements, between British and Swedish fall-cone methods are presented in Tab. 1. The difference is in interpretation of the test (Swedish method uses semi logarithmic plot, whereas British uses an arithmetic plot). Liquid limit of soft grained soils is obtained at the moisture content, at which the value of undrained shear strength of soil is about 1.6 kPa for both cones.

Tab. 1. Main differences between 80 g / 30° and 60 g / 60° fall cone methods

	80 g / 30°	60 g / 60°
Range of penetration	15 to 25 mm	7 to 15 mm
max. difference between two successive tests	0.5 mm	0.4 mm
w_L , determined at penetration of	20 mm	10 mm

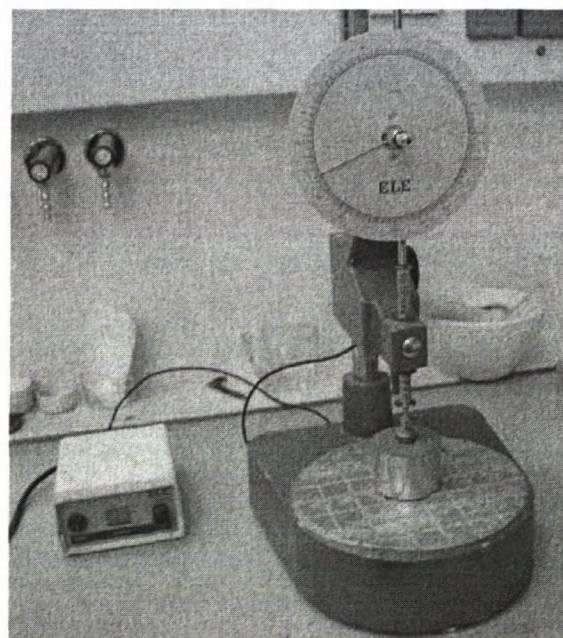
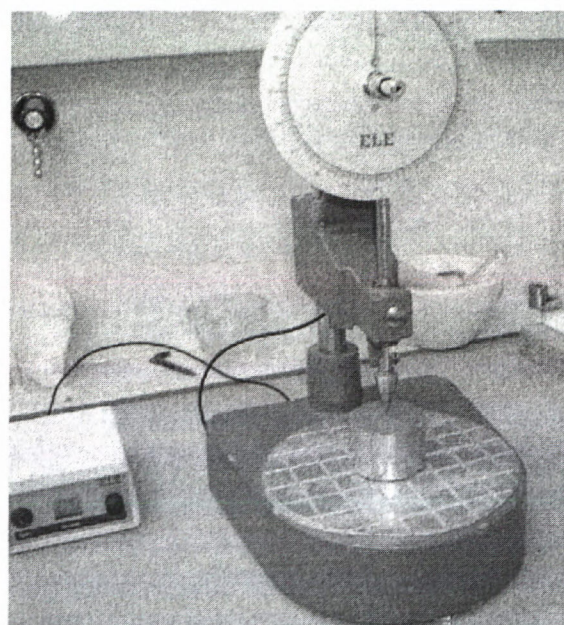


Fig. 2. Fall-cone device before and after penetration test.

Fig. 2 shows an apparatus for performance of the fall-cone liquid limit test 80 g / 30° cone before penetration (up) and after penetration (down). An important requirement for the test is represented by the free fall of the cone and the penetration measurement with desired accuracy. British method allows the linear graphical interpretation of dependence of moisture content on penetration. Penetration range of the Swedish fall-cone from 7 to 15 mm corresponds to penetration range from 14 to 30 mm of the British fall-cone. Penetration range of the British fall-cone between 15 and 25 mm corresponds to penetration range between 7.5 and 12.5 mm of the Swedish fall-cone (Farrell et al., 1999). From this comparison there follows that liquid limit determined by the British fall-cone is specified from narrower range of moisture content of soils. One-point penetration method should be therefore more accurate by the use of the British fall-cone. One-

point penetration method applies only for one value of liquid limit (one penetration) multiplied by empirically determined correction factor. This method could only be used in the case of very little amount of soil, considering this method not accurate and yielding only approximate results. Technical specification CEN ISO/TC 17 892-12:2005 does not mention this method, because of above mentioned reasons.

3. Comparison of Casagrande method for the liquid limit determination with fall-cone method

Casagrande method is an alternative method for liquid limit determination according to CEN ISO/TC 17892-12:2005. The technical specification states, that the results are dependent on the construction of the apparatus and the skills of laboratory worker (worker performing the test). Besides this, Casagrande type apparatus and the testing method itself underwent small, but significant changes from the time when Casagrande first designed them. These changes caused differences in values of liquid limit determined by this method. Casagrande method is based on the proposition, that the shear strength of all samples on the liquid limit must have constant value. According to our measurements, which are in line with Leroueil's (1996) and other authors' knowledge, undrained shear strength at the moisture content on the liquid limit decreases with increasing liquid limit. According to Leroueil (1996) the values are from 2.8 to 1.2 kPa. This fact is the reason why there are differences between liquid limit values determined by Casagrande method and fall-cone method.

According to the experiences in countries where the fall-cone method is used, this method is much more suitable for the liquid limit determination than Casagrande method. It is less bent by subjective errors of laboratory worker. According to British standard BS 1377: Part 2 (1990), the differences between results obtained by Casagrande method and fall-cone method are low for liquid limits less than 100 %. Fig. 3 shows the results of

comparison of the liquid limit values determined by Casagrande apparatus and fall-cone method 60°/60g according to Karlsson (1981) and institutions BAW and BRE (Farrell, 1998).

Fig. 4 shows the results of comparison of liquid limit values determined by Casagrande apparatus and fall-cone method 60°/60 g according to Karlsson (1981) and several other authors. Ladeire (1995) compared liquid limits by British fall-cone and Casagrande apparatus and found a relationship

$$w_{LCasagrande} = w_{LFall\ cone} - 3,$$

which means that the liquid limit determined by fall-cone is 3 % less than the liquid limit determined by the Casagrande method. This is in contradiction to our measurements, shown in the article and in the results in Fig. 3.

4. Results of laboratory investigation in Slovakia

There were performed laboratory tests for determination of liquid limit by Casagrande method and Fall-cone method on samples of low-plasticity, medium-plasticity, high, very high and extremely high-plasticity in the Laboratory of engineering geology of State geological Institute of Dionýz Štúr. The British cone (80g/30°) was used for the determination of liquid limit by fall-cone method. The number of tested soil samples was 138. The samples were divided into two sets. The first set of tested soil samples has the interval of water content on the liquid limit from 19 % to 90 % (108 samples). The second set contains samples of liquid limit higher than 90 % (28 samples). The results of 108 tests carried out on samples with the liquid limits up to 90 % are shown in Fig. 5. The regression lines were determined separately for low-plasticity ($w_L < 35\%$), medium-plasticity ($w_L = 35-50\%$), high-plasticity ($w_L = 50-70\%$), and very high plastic soils ($w_L = 70-90\%$). These equations of linear correlation line were determined for the relationship between $w_{LCasagrande}(\%)$ by Casagrande method and $w_{LFall\ cone}(\%)$ performed by fall-cone method.

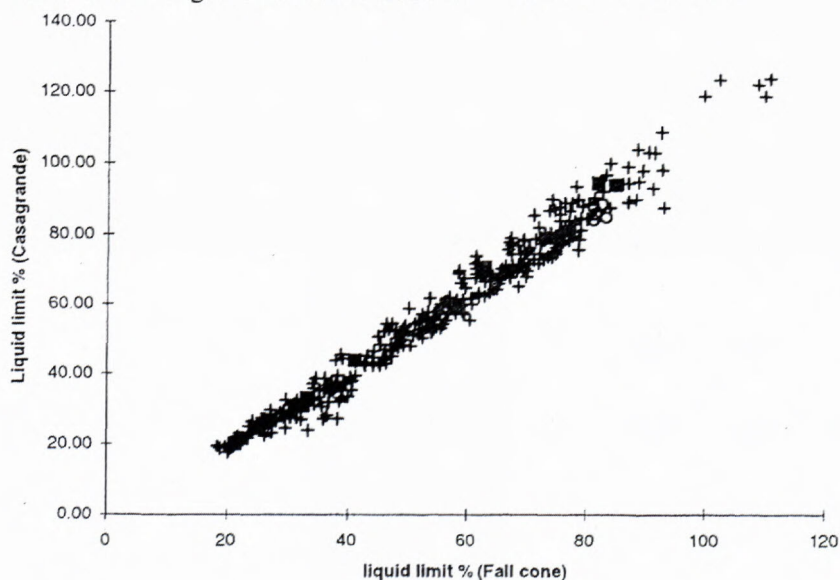


Fig. 3. Comparison of liquid limits by Casagrande and fall-cone methods (in Farrell, 1998).

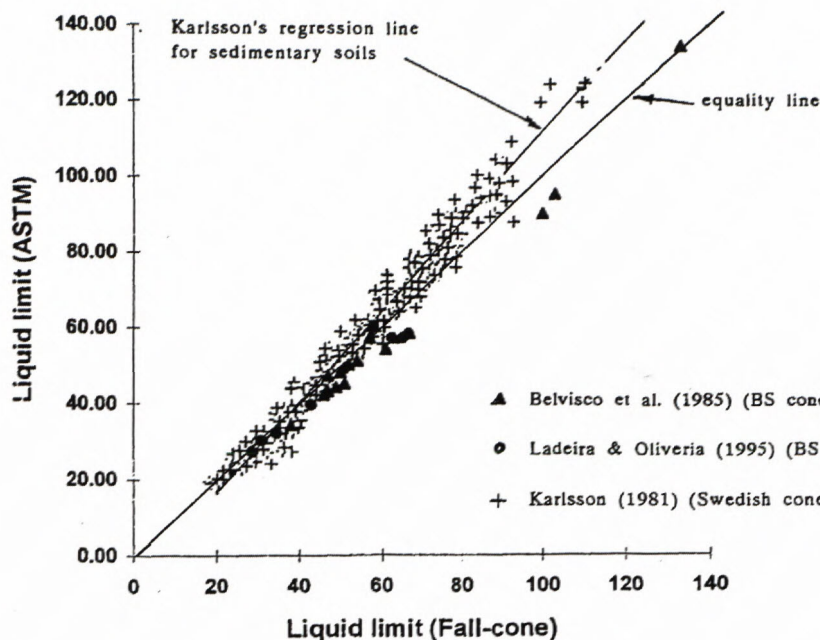


Fig. 4. Comparison of liquid limits by Casagrande and fall-cone methods (in Farrel, 1995).

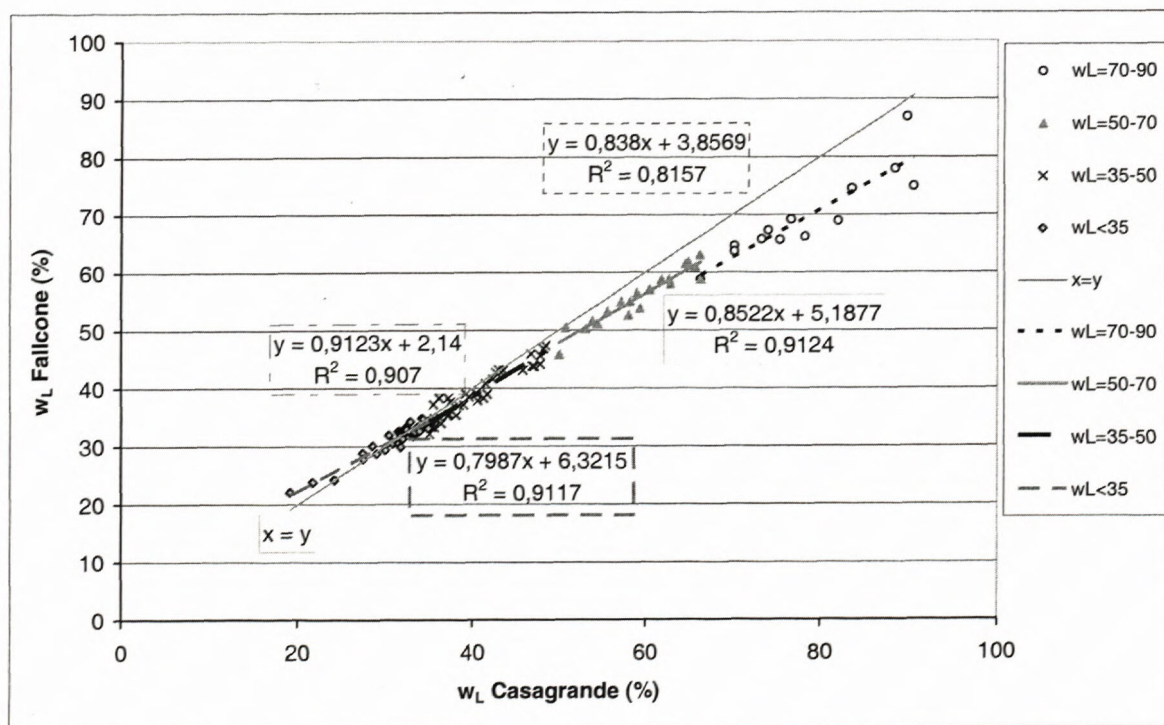


Fig. 5. Comparison of liquid limits by Casagrande and fall-cone methods for $w_L < 90\%$, separately for soils with low, medium, high and very high plasticity.

The equation for regression line for low plastic soils with $w_L < 35\%$ is:

$$w_{L\text{Fall cone}} = 0.7987 \times w_{L\text{Casagrande}} + 6.3215 \quad R = 0.955 \quad (1)$$

The equation for line for medium-plastic soils with $35 < w_L < 50\%$ is:

$$w_{L\text{Fall cone}} = 0.9123 \times w_{L\text{Casagrande}} + 2.14 \quad R = 0.952 \quad (2)$$

The equation for line for high-plastic soils with $50 < w_L < 70\%$ is:

$$w_{L\text{Fall cone}} = 0.8522 \times w_{L\text{Casagrande}} + 5.1877 \quad R = 0.955 \quad (3)$$

The equation for line for very high-plastic soils with $70 < w_L < 90\%$ is:

$$w_{L\text{Fall cone}} = 0.838 \times w_{L\text{Casagrande}} + 3.8569 \quad R = 0.903 \quad (4)$$

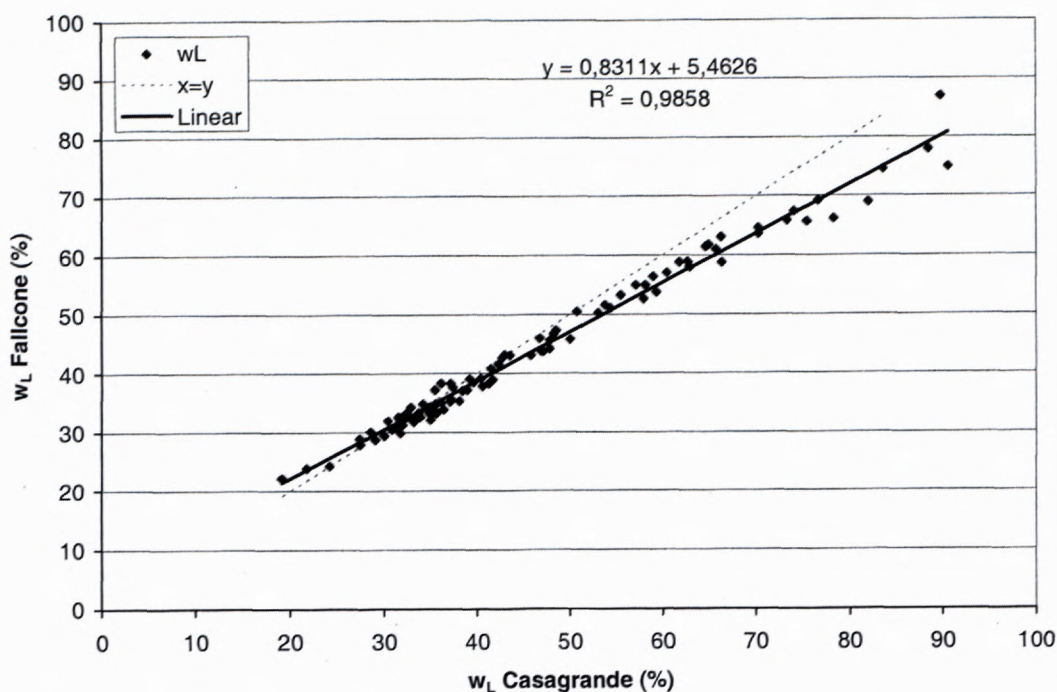


Fig. 6: Comparison of liquid limits by Casagrande and fall-cone methods for $w_L < 90\%$

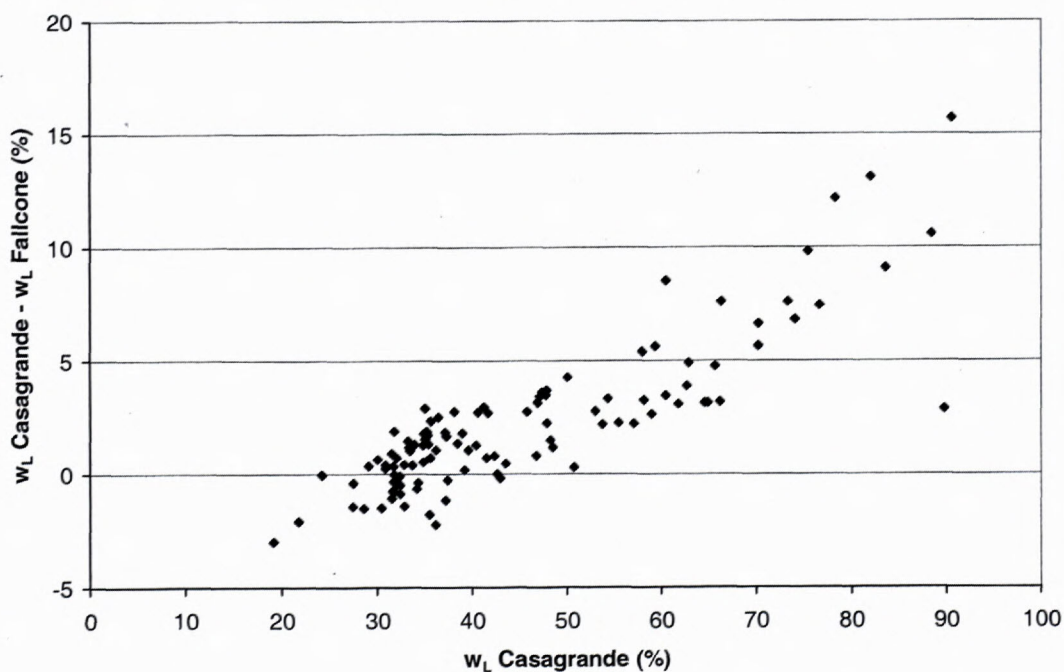


Fig. 7: Differences in liquid limits by Casagrande and fall-cone methods for $w_L < 90\%$.

The comparison of liquid limits by Casagrande and fall-cone methods for samples with $w_L < 90\%$ shows very good correlation as shown in Fig. 6. The equation from statistical analyses for the relation between $w_{LCasagrande}(\%)$ determined by Casagrande method and $w_{LFall\ cone}(\%)$ determined by fall-cone method, with the value of correlation coefficient of 0.993 is:

$$w_{LFall\ cone} = 0.8311 w_{LCasagrande} + 5.463 \quad (5)$$

Liquid limit determined by the fall-cone method is higher than the liquid limit determined by the Casagrande

method for values up to w_L of 30 %. Liquid limits for values between 30 % and 50 % showed a very good correlation and differ within very small and acceptable limits. Liquid limit determined by the fall-cone is lower than the liquid limit determined by the Casagrande method for values higher than 50 %. This is documented on Fig. 7, which shows a percentage difference between liquid limit values determined by both methods. For better imagination of the particular methods, a comparison of liquid limits of samples from the different localities around Slovakia, by the use of regression equation (5), is shown in Tab. 2.

Tab. 2. Values of fall-cone liquid limits determined using equation (1).

$w_{LCasagrande}$ (%) Casagrande method	$w_{LFall\ cone}$ (%) Fall-cone method
20	22
25	26
30	30
35	35
40	39
45	43
50	47
55	51
60	55
70	64
80	72
90	80

Fig. 8 shows graphical comparison of liquid limits of all samples with w_L over 90 %. An equation for the relationship between w_L (%) determined by Casagrande method and w_L determined by fall-cone method was statistically determined:

$$w_{LFall\ cone} = 0.6714 w_{LCasagrande} + 28.923 \quad (6)$$

Correlation coefficient R is 0.9945.

Fig. 9 shows the distribution of liquid limit values determined by both methods, which linearly increases with the increasing value of liquid limit determined by Casagrande method.

4. Conclusion

Atterberg limits are very useful characteristics of fine-grained soil state to determine soil behaviour. Different geotechnical properties, for example soil strength, undrained shear strength, compressibility or optimum water content, can be derived from correlations with the liquid, or plastic limits.

Practically all determined liquid limits in Slovakia are obtained by the Casagrande method. Because of testing procedures (methodology) harmonization in the whole region of European Union to obtain as comparable and reproducible data as possible, it is recommended to prefer fall-cone method for liquid limit of soil determination. The Eurocode 7, part 2 recommends the use of two types of cones: cone 60g/60° (Swedish) and also 80g/30° (British) and allows the use of Casagrande method. We suppose that after a certain temporary period the fall-cone penetration will be commonly used in most of laboratories in Slovakia. Procedure of sample preparations for both methods is the same. The amount of soil needed for the test performance is bigger for the fall-cone method, which requires about 200 g of soil. Fall-cone method is not faster, but is more accurate, because the mechanism of test depends directly on the static shear strength of soil. There is a dynamic element involved in testing by the Casagrande method, which does not depend on the shear strength in the same way for all types of soils. Undrained shear strength at the liquid limit decreases with increasing liquid limit, which is the reason of the different results of liquid limit values determined by Casagrande and fall-cone methods.

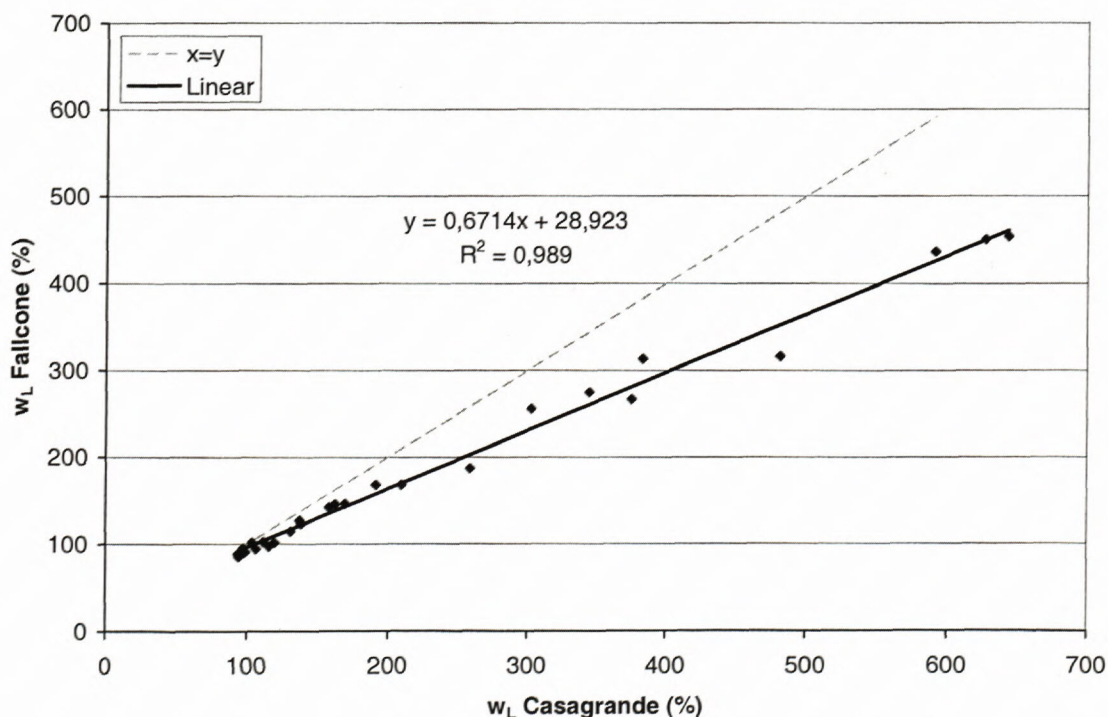


Fig. 8. Comparison of liquid limits by Casagrande and fall-cone methods for $w_L > 90\%$.

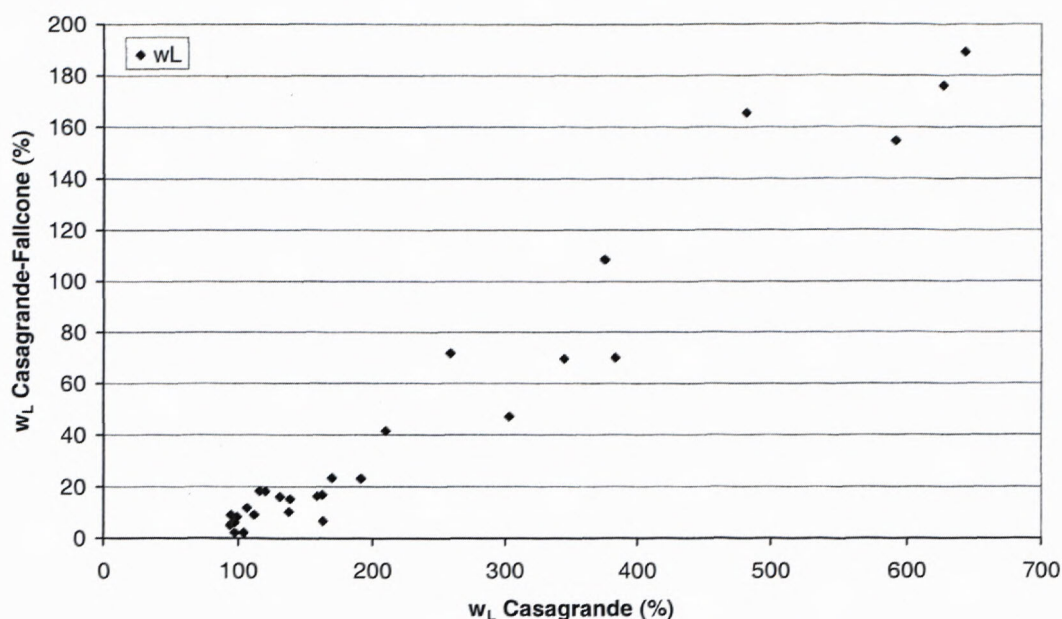


Fig. 9. Differences in liquid limits by Casagrande and fall-cone methods for $w_L > 90\%$.

From the practical point of view the way of liquid limit determination for most of soils in Slovakia, clays and silts with low and medium plasticity, is negligible. There is close correlation for soils with liquid limit between 30 and 50 %. There are significant differences between liquid limits determined using Casagrande and fall cone devices for soils with the very high and extremely high plasticity. It is necessary to know the comparison of results from particular methods, to be able to use previous liquid limit values determined by the Casagrande method in future and to know how to interpret them together with the values determined by the fall-cone method. In the article, there is presented the linear regression line for liquid limit values determined by Casagrande apparatus and fall-cone 80g/30° method for samples with liquid limit less than 90 % and for soil samples with liquid limit over 90 %, extremely plastic soils, obtained on the base of laboratory tests of soil samples from different localities in Slovakia. It is necessary to continue collecting results of liquid limit determination by both methods in future to obtain as good correlation of investigated methods as possible.

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